VOL. XIX. NOVEMBER, 1897. No. 9.

AMERICAN CHEMICAL JOURNAL.

THE ACTION OF CARBON DIOXIDE UPON SODIUM ALUMINATE AND THE FORMATION OF BASIC ALUMINIUM CARBONATE.

BY WILLIAM C. DAY.

The literature of aluminium carbonate is intimately associated with that of ferric and chromic carbonates. The existence of carbonate of aluminium and of the corresponding ferric and chromic compounds is referred to as doubtful by high authorities at the present time. The writer cannot help feeling, however, that this doubt is carried further in the minds of many chemists of to-day than a careful study of the literature will justify, and certainly further than the results of experience in connection with the present investigation would warrant. Patents have been issued upon processes for obtaining alumina from sodium aluminate based upon the assumption that carbon dioxide acts at once upon sodium aluminate in the sense of the following equation:

$$Al_2O_3(ONa)_2 + CO_2 + 3H_2O = Al_2(OH)_6 + Na_2CO_3.$$

Thus in a process originally patented by Le Chatelier this reaction is assumed, but in connection with a description of it is the statement that alumina thus precipitated always contains a certain quantity of alkaline carbonate which cannot be removed by washing with water. It may, however, be separated by digestion with the aid of heat in a small quantity of

dilute hydrochloric or nitric acid, or by digestion with chloride of aluminium in excess. That the reaction written above does not take place is, I believe, thoroughly proved by the results of the present investigation.

Investigators having for their object the preparation of aluminium carbonate have generally followed the plan of adding alkaline carbonates in solution to solutions of alum or other aluminium salt, and then studying the resulting precipitate. No one, so far as I know, has investigated the product formed by passing carbon dioxide into a cold solution of an alkaline aluminate.

Berzelius[1] says, "if alumina is precipitated by an excess of alkaline carbonates, the precipitate is an insoluble double salt of alkaline carbonate and alumina, which dissolves in acids with effervescence." He, as well as Bucholz before him, doubted the existence of aluminium carbonate.

H. Bley[2] studied the action of alkaline carbonates in excess upon solutions of alum and sulphate of aluminium. According to this writer, either a basic carbonate of aluminium or a double salt of basic aluminium carbonate and the alkaline carbonate employed is obtained. Referring to the assertion that such precipitates continually contain alkaline carbonate mechanically held, he says, "I have convinced myself by the most careful investigation that they are in many cases quite free from alkaline carbonate."

The precipitates studied by Bley were prepared by the use of both ammonium and potassium carbonates. His method of analysis was not clearly shown, but in stating the results he gives the weights of carbon dioxide and alumina only, thus indicating that water was determined by difference.

One preparation gave the following figures:

I. Al_2O_3, 46.70; CO_2, 6.77; H_2O, 46.53.
II. " 47.80; " 5.50; " 46.70.

Another preparation (using potassium carbonate) showed the following percentage composition:

I. Al_2O_3, 49.50; CO_2, 6.37; H_2O, 44.12.
II. " 46.00; " 5.27; " 48.73.

[1] Lehrbuch der Chemie, 5te Aufl. Bd. 3, 479.
[2] J. prakt. Chem., 1846, 39, 1.

A third precipitate contained :

I. Al_2O_3, 45.43 ; CO_2, 6.54 ; H_2O, 48.02.
II. " 48.20 ; " 11.39 ; " 40.41.

Inspection of these figures reveals a lack of agreement between two analyses of the same preparation, which is hardly calculated to inspire confidence in either the method of analysis employed or the manipulation.

Bley regards all such precipitates as "mere mixtures."

In 1854 Heinrich Rose published a paper "on the influence of water in chemical decompositions." In this paper reference is made to the work of Muspratt who, without referring to the work of Bley, prepared and analyzed a compound with the following results : Al_2O_3, 44.86 per cent. ; CO_2, 12.91 per cent. ; H_2O, 42.23 per cent.

In the course of his paper, Rose[1] says "it is difficult to see how an alkaline carbonate in solution added to a solution of another salt can be contained mixed in the washed precipitate obtained." Rose obtained the precipitate analyzed by him by treating potassium and ammonium alums mixed in solution with ammonium carbonate in excess. The precipitate was washed with water until the wash-water showed no trace of sulphuric acid. In spite of this, however, on dissolving a sample in dilute hydrochloric acid, a heavy precipitate was obtained with barium chloride. The precipitate was all dissolved in hydrochloric acid, and obtained again by means of ammonium carbonate from this solution. Washing was continued until all traces of sulphuric and hydrochloric acids were removed. Treated with hydrochloric acid, carbon dioxide was freely evolved. On heating, a strong odor of ammonia was produced. Analysis gave the following result from which a formula was deduced :

Al_2O_3, 34.48 ; ammonium oxide, 15.33 ; CO_2, 26.77 ; H_2O, 23.42.

This compound appears then to have been a double carbonate of aluminium and ammonium.

In 1856 M. Langlois[2] published the results of a study of carbonates of aluminium, iron, and chromium. The following

[1] Poggendorf's Annalen, **91**, 452.
[2] Annales d. ch. et d. phys. [3], **48**, 502.

quotation from this paper is of much interest: "When we add an alkaline carbonate to a solution of an aluminium salt, a precipitate is obtained and, at the same time, the disengagement of carbon dioxide is observed. It is generally believed that this precipitate is nothing but alumina, still retaining a little alkaline carbonate to which is due the effervesence with acids. I have repeated this experiment, and am assured that by washing with a sufficient quantity of water the precipitate can be entirely freed from alkaline salt. It continues nevertheless to effervesce, which proves that a part of the alumina remains combined with the carbonic acid. The same has been remarked by M. Bley:[1] "There is unquestionably produced a very basic compound of carbonic acid and aluminium hydroxide. This compound is destroyed at a temperature which does not exceed 100°."

This precipitate, upon analysis, gave the following result: Al_2O_3, 48.80 per cent.; CO_2, 7.72 per cent.; H_2O, 43.48 per cent.

On the basis of this analysis the following formula was proposed:

$$3(Al_2O_3.CO_2) + 5(Al_2O_3.8HO).$$

Langlois does not appear to have determined each of the three constituents directly; the water seems to have been determined by difference. The operations described seem to have been carried out with great care and thoroughness and the whole investigation seems highly trustworthy.

In 1858 Wallace[2] published the results of an investigation of aluminium, iron, and chromium carbonates. In this he refers to the fact that the existence of such carbonates has been denied by several authorities. The precipitates investigated were prepared by adding sodium carbonate to a dilute solution of aluminium chloride. He emphasizes the tedious character of the work and refers to the time required for washing and drying in terms of weeks. Notwithstanding this protracted washing he was unable to remove all alkali which he assumed to be present in the form of sodium bicarbonate, and calculated his analytical results upon the weight of material

[1] *Loc. cit.* [2] Chem. Gazette, **16**, 410.

taken minus the calculated weight of sodium bicarbonate. Inasmuch as the amount of sodium oxide found is not stated, the reader is left unable to draw any conclusions for himself and the results necessarily lose interest to some extent.

He concludes from the analysis of several preparations that protracted washing decomposes the aluminium carbonate in some degree.

His analytical results, calculated as explained above, are the following:

Al_2O_3, 56.19; CO_2, 14.26; H_2O, 29.55.

From these figures he calculated the formula,

$$3Al_2O_3.2CO_2 + 9HO = 2(Al_2O_3CO_2 + 3HO) + Al_2O_3.3HO.$$

This formula would require Al_2O_3, 55.04; CO_2, 15.83; H_2O, 29.13 per cent. He explains the deficiency of carbon dioxide in the substance analyzed as due to decomposition from protracted washing.

In 1860 James Barratt[1] investigated the carbonates of aluminium, iron, and chromium.

He refers to the work of Wallace, just considered, also cites Saussure as authority for the belief that the reputed carbonate of aluminium contains no carbon dioxide at all. He claims to have prepared the compound precisely in the same manner as prescribed by Dr. Wallace. After washing it for two days it was dried and analyzed. Three per cent. of carbon dioxide was found. He then triturated it in a mortar with water, placed it upon a filter, and washed further and dried as before over sulphuric acid. Analysis gave these results:

	Calculated for $Al_2(OH)_6$.	Found.
Al_2O_3	65.384	65.03
H_2O	34.616	34.97
CO_2	....	none
	100.000	100.00

Commenting upon these results, he says: "From the above it is evident that when an aluminium salt is precipitated by an alkaline carbonate there is no carbonate of aluminium formed. The three per cent. of carbonic acid found in the first instance

[1] Chem. News, 1860, 1, 110.

was in all probability due to the retention of some of the precipitant (carbonate of soda) by the hydrated alumina."

His study of the carbonates of iron and chromium showed the presence of carbon dioxide in both, and formulæ including carbon dioxide were calculated for these. The paper concludes as follows:

"The preceding examinations were all most carefully performed under the direction of Dr. Muspratt who, with myself, cannot account for the whole of the carbonic acid being removed from the alumina and not from the other two oxides; such, however, is the fact as proved by the foregoing experiments, all of which were conducted on the same plan, and each precipitate was apparently submitted to the same conditions and treatment."

In 1862 appeared a publication "On the carbonates of alumina, glucina, and the sesquioxides of iron, chromium, and uranium," by Theodore Parkman.[1] After some difficulty in preparing and washing the precipitates obtained by the action of sodium carbonate upon potassium alum, the author finally adopted the plan of washing with water, saturated with carbonic acid, until a portion of the filtrate, after being boiled to expel carbonic acid, gave no alkaline reaction. This, he says, would probably give correct results since the water being already saturated with carbon dioxide would hardly wash out any from the substance. None of the precipitates were dried before analyzing so that only the percentages of alumina and carbon dioxide were obtainable. The method of analysis was to introduce the substance (which had been previously under pressure between folds of paper for about twelve hours) into a bulb-tube of hard glass. The whole was weighed, connected with a weighed calcium-chloride tube, and ignited in a slow stream of dry air. The loss of weight of the bulb-tube and contents minus the increase of weight of the calcium-chloride tube would give the weight of the carbon dioxide.

The following analyses express merely the ratios of alumina and carbon dioxide, and were obtained simply by adding to-

[1] Silliman's Journal, [3], **34**, 321.

gether the weights of carbon dioxide and alumina and dividing the weight of each constituent by the sum :

	Prep. I.		Prep. II.	Prep. III.		Prep. IV.	
	I.	II.		I.	II.	I.	II.
Al_2O_3	79.13	79.32	79.95	81.37	81.91	77.51	76.72
CO_2	20.87	20.68	24.05	18.63	18.09	22.49	23.28

Commenting upon these figures the author says, "the precipitate by the fixed alkaline carbonates in salts of alumina varies in composition, but approaches the formula $Al_2O_3.CO_2$, and is probably a mixture of this with a more basic salt." While the above figures are interesting, it must be remembered that they represent the partial composition of a wet material, and are therefore scarcely comparable with results obtained from the complete analysis of air-dried substances, such as are treated of in other investigations.

In 1879, Urbain and Renoul[1] published the results of a research "on a compound of alumina with carbonic acid." In the course of the paper appear the following statements: "In the preparation of alumina by means of sodium carbonate and alum, two bodies, very different in appearance, can be obtained according as the precipitation is effected at the boiling-point or at the surrounding temperature. In the first case the precipitate is gelatinous and transparent, and filters with difficulty; in the second case, on the contrary, it is opaque, and separates from the liquid with the greatest ease. In the dry state the same difference exists. Alumina prepared hot is hard and like horn in appearance; the alumina obtained cold is pulverulent and perfectly white. Brought in contact with a solution of coloring matter, for example an infusion of campeche wood, the opaque alumina absorbs twice as much coloring matter as the gelatinous.

"When alumina prepared in the cold is treated with an acid it dissolves immediately, giving rise to an abundant liberation of carbonic acid, while alumina precipitated at 100° dissolves only slowly and with no production of gas."

This precipitate was obtained from aluminium sulphate as well as from alum, and by the use of ammonium carbonate instead of sodium carbonate; the precipitate had the same properties

[1] Comptes rendus, 88, 1133.

and nearly the same composition, regardless of the method of obtaining it. Dried over sulphuric acid until the weight no longer changed, the substance showed the following composition:

Al_2O_3, 52; CO_2, 11; H_2O, 37, corresponding to the following formula, $CO_2.2Al_2O_3.8HO$.

"The substance is destroyed by heat; even at 30° it commences to lose its carbonic acid. When it is placed in water and this is warmed, a disengagement of acid is observed, which increases with the temperature, and is complete after boiling some time. Thus, contrary to what has heretofore been supposed, alumina is capable of combining with carbonic acid and forming, it is true, a compound of marked instability."

The observations made in the paper just considered more nearly agree with those made by the writer than the descriptions contained in any other of the publications on the subject.

In 1893 A. Ditte[1] published the results of a study of the action of carbon dioxide upon aluminates of the alkalies in which he obtains crystallized alumina (Gibbsite). He says "when potassium carbonate is added, drop by drop, to a solution of potassium aluminate, a precipitate forms which at first redissolves, but afterwards becomes permanent; it has perhaps the composition $3K_2O.Al_2O_3.5CO_2$." No analyses of the compounds are given and the reasons for ascribing this formula to the precipitate do not appear in the paper. The following explanation of the action of carbon dioxide upon alkaline aluminate is of interest. "If carbonic anhydride is passed into a solution of potassium aluminate containing a small excess of alkali until a permanent precipitate of the double carbonate and the crystallized hydroxide begins to form, and the flask is then closed, a heavy precipitate of the double carbonate at first settles out, but this is gradually decomposed by the potassium hydroxide liberated by the decomposition of the aluminate by water, and crystallized aluminium hydroxide separates. If the solution contains a considerable excess of alkali, and carbonic anhydride is passed

[1] Comptes rendus, **116**, 183–185 and 386–388.

into it until a permanent precipitate begins to form, and the flask is then closed, a precipitate of the double carbonate separates, but, as there is still sufficient potassium hydroxide in the liquid to prevent decomposition of the aluminate, crystallized aluminium hydroxide is not formed." This paper is interesting and suggestive, but it does not deal directly with the issues of the present investigation, inasmuch as no analyses of precipitates obtained are given, and the question of the existence of carbonate of aluminium is not considered as a distinct issue.

Some time ago, being desirous of obtaining pure alumina by the action of carbon dioxide upon sodium aluminate, the writer carried out some experiments with this end in view and, in the course of the work, became thoroughly impressed with a sense of the difficulty of washing the precipitated alumina free from alkaline carbonate, and also by the observation that the precipitate did not look like ordinary alumina in that it appeared somewhat less gelatinous or rather more granular, and that its color was a more opaque white than that of alumina as obtained by precipitation by ammonia from alum or other aluminium salt. It seemed, therefore, advisable to carry out a series of experiments with the object of determining by quantitative analysis the exact nature of the carbon dioxide precipitate after it had been washed until water would remove nothing more. Consultation of a number of reference works, including Watts' Dictionary, showed that the existence of carbonate of aluminium was a matter of doubt. No further study of the literature was undertaken until the investigation was finished.

The sodium aluminate employed was obtained from a natural phosphate of iron and aluminium known by the trade-name of "Connetable" phosphate rock. This was treated with quicklime and sodium carbonate in the presence of water sufficient to form a thick mud, and the resulting sodium aluminate was afterwards washed out, leaving all iron compounds and phosphate of calcium undissolved, the aluminate containing no trace of phosphoric acid. Carbon dioxide was then freely passed through the solution of aluminate until no more precipitate resulted.

Before taking up these experiments a specimen of alumina, described in the catalogue of a dealer in chemicals as "alumina soluble in acids," was studied. This, on treatment with dilute acids, dissolved promptly but with liberal effervescence. The method of analysis followed in this and all other cases consisted in heating the substance in a combustion tube placed in a combustion furnace. The water and carbon dioxide expelled by heat were absorbed in weighed calcium-chloride tubes and caustic-potash bulbs, respectively, placed just as in the determination of hydrogen and carbon in an organic analysis. Alumina was in all cases determined by dissolving the original substance in acid and precipitating aluminium hydroxide by means of ammonia in the customary manner. Sodium was determined by evaporating the filtrate from the alumina to dryness, and weighing finally as sodium sulphate, or by determining volumetrically the chlorine present in combination with sodium as sodium chloride and calculating the sodium corresponding thereto.

Analysis of Commercial Alumina "Soluble in Acids."

I. 0.5036 gram substance gave 0.1351 gram CO_2, and 0.1029 gram H_2O.

II. 0.2487 gram substance gave 0.0645 gram CO_2, and 0.0498 gram H_2O.

III. 0.2231 gram substance gave 0.07126 gram Al_2O_3, and 0.1097 gram Na_2SO_4.

IV. 0.2180 gram substance gave 0.6826 gram Al_2O_3, and 0.1055 gram Na_2SO_4.

	I.	II.	III.	IV.
CO_2	26.83	25.93	....	....
H_2O	20.43	20.02	....	....
Al_2O_3	....	....	31.94	31.31
Na_2O	....	....	21.47	21.12

Averaging these results we have the following composition for alumina "soluble in acids:"

	Per cent.
CO_2	26.38
H_2O	20.23
Al_2O_3	31.63
Na_2O	21.30
	99.54

Evidently alumina is a misnomer for such a mixture as is indicated by these figures.

Ten grams of this material were then washed with boiling water until the washings gave no alkaline reaction with litmus or phenol phthalein. The residue from this washing effervesced upon treatment with dilute hydrochloric acid, but it did not dissolve so completely as before washing, nor could it be entirely dissolved by dilute acid even upon heating.

After drying upon the water-bath it was analyzed :

I. 0.2129 gram substance gave 0.0366 gram CO_2, and 0.0471 gram H_2O.

II. 0.2062 gram substance gave 0.0361 gram CO_2, and 0.0464 gram H_2O.

III. 0.2105 gram substance gave 0.10276 gram Al_2O_3, and 0.0562 gram Na_2SO_4.

IV. 0.2169 gram substance gave 0.10616 gram Al_2O_3, and 0.0635 gram Na_2SO_4.

	I.	II.	III.	IV.
CO_2	17.19	17.51	....	....
H_2O	22.12	22.50	....	....
Al_2O_3	....	....	48.82	48.94
Na_2O	....	....	11.66	12.78

Averaging these we have :

CO_2	17.35
H_2O	22.31
Al_2O_3	48.88
Na_2O	12.22
	100.76

The amount of carbon dioxide required by 12.22 parts by weight of sodium oxide to form sodium bicarbonate is 17.34. The substance having been washed with hot water it seems strange that sodium bicarbonate should have survived such treatment. As is well-known, it is difficult to preserve sodium bicarbonate even at ordinary temperatures, without partial decomposition into the normal carbonate. The question naturally arises, Is the carbon dioxide here present held in combination by the oxide of sodium only, or does the weak base alumina also play a part in this ?

Preparation A from Connetable Phosphate Rock.

This was made by heating powdered Connetable rock with quicklime and sodium carbonate in the presence of enough water to form a thick mud, and subsequently washing out the sodium aluminate thus formed with hot water. The solution so obtained contained no trace of phosphoric acid. It was poured into bottles and a rapid current of carbon dioxide was passed through the cold liquid until no alumina could be found in the solution.

After the carbon dioxide had been passing through the solution for some little time a precipitate began to form; this could at first be redissolved by shaking, but later it became permanent. The precipitate settled quite readily, and differed from aluminium hydroxide, precipitated by ammonia from a solution of an aluminium salt, in that it was of an opaque white color and more granular or less gelatinous than the hydroxide as ordinarily obtained. The precipitate was washed with hot water upon the filter, after which it was dried on the water-bath. The dried substance was then washed with hot water by decantation until the washings were no longer alkaline. After drying again on the water-bath, treatment of a portion with hydrochloric acid caused effervescence, and washing with hot water produced an alkaline filtrate. It was evident that drying on the water-bath had had the effect of rendering alkaline matter soluble, since, before this drying, no alkali was detected in the wash-water. Washing was again resorted to; the substance was shaken with hot water, and allowed to settle twenty-four times before a neutral filtrate was obtained. After a final drying on the water-bath, it still effervesced with dilute hydrochloric acid. Subjected to analysis it gave the following results:

I. 0.5026 gram substance gave 0.1231 gram CO_2, and 0.1122 gram H_2O.

II. 0.2396 gram substance gave 0.0598 gram CO_2, and 0.0507 gram H_2O.

III. 0.2012 gram substance gave 0.07636 gram Al_2O_3, and 0.0794 gram Na_2SO_4.

IV. 0.5043 gram substance gave 0.19206 gram Al_2O_3, and 0.2030 gram Na_2SO_4.

	I.	II.	III.	IV.
CO_2	24.49	24.95	....	....
H_2O	22.32	21.16	....	....
Al_2O_3	....	....	37.95	38.08
Na_2O	....	....	17.19	17.57

Averaging the results, we obtain for preparation *A* the following percentage composition :

	Per cent.
CO_2	24.72
H_2O	21.74
Al_2O_3	38.02
Na_2O	17.38
	101.86

The amount of carbon dioxide required by 17.38 parts of sodium oxide is 24.66, if we assume that the carbon dioxide present is combined only with oxide of sodium to form sodium bicarbonate ; this is very nearly the amount of carbon dioxide actually found, but, as in the preceding preparation, it seems strange that sodium bicarbonate should be able to withstand such protracted washing with hot water as well as repeated drying at the temperature of boiling water.

Preparation B from Connetable Rock.

Wishing to avoid any decomposition such as might be caused by heat, it was decided at this point to conduct all washings of the precipitated alumina with cold water, and to allow the completely washed precipitate to dry in the air without any heating whatever. The material was prepared from Connetable rock in the same manner as *A*. After siphoning off the clear liquid from the carbon dioxide precipitate, the latter was washed with cold water by decantation. During the first two washings the precipitate settled rapidly and completely ; at the third addition of water it settled much more slowly and, even after standing over night, it had not settled entirely, but the supernatant liquid was slightly turbid. After three more washings it again settled quickly and perfectly. This stage of slow settling was noticed in all the subsequent preparations, *i. e.*, they settled quickly and perfectly for the first three or four washings, then much more slowly

and less perfectly for several washings, after which rapid and complete settling again took place. After seven washings, phenol phthaleïn gave no indication of alkalinity in the wash-water; the precipitate was then drained off, and spread out in the air to dry. When perfectly dry, it was powdered and analyzed with the following results:

I. 0.1485 gram substance gave 0.0130 gram CO_2, and 0.0588 gram H_2O.

II. 0.2090 gram substance gave 0.0195 gram CO_2, and 0.0817 gram H_2O.

III. 0.1088 gram substance gave 0.0099 gram CO_2, and 0.0425 gram H_2O.

IV. 0.1571 gram substance gave 0.0771 gram Al_2O_3, and 0.0107 gram Na_2SO_4.

V. 0.1657 gram substance gave 0.0824 gram Al_2O_3, and 0.0080 gram Na_2SO_4.

VI. 0.1704 gram substance gave 0.0850 gram Al_2O_3, and 0.0091 gram Na_2SO_4.

	I.	II.	III.	IV.	V.	VI.
CO_2	8.75	9.33	9.1	....	....	....
H_2O	39.59	39.09	39.06	....	....	....
Al_2O_3	....	....	....	49.08	49.73	49.88
Na_2O	....	....	....	2.97	2.11	2.33

From an average of these results the following percentage composition is indicated.

CO_2	9.06
H_2O	39.25
Al_2O_3	49.56
Na_2O	2.47
	100.34

This preparation dissolved promptly and completely in dilute acid, and with effervescence.

The 2.47 per cent. of sodium oxide here present require, in order to form sodium bicarbonate, 3.51 per cent. of carbon dioxide, whereas the amount of carbon dioxide actually present is 9.06 per cent., or 5.55 more than the maximum with which the sodium oxide is capable of combining. There seems to be no way of avoiding the conclusion that in this compound

5.55 per cent. of carbon dioxide is held in combination by alumina, and that we have in this material either a basic double carbonate of sodium and aluminium or aluminium carbonate mixed with other compounds.

Preparation C from Connetable Rock.

This was made according to the method adopted for *A* and *B*. As in the case of *B*, washing was done with cold water only, and the material was air-dried. The precipitate settled promptly, leaving the wash-water perfectly clear for the first four washings; then, as in the other cases, it reached the slow-settling stage, when for three washings it settled very slowly, after which it again settled promptly each time. When phenol phthaleïn failed to indicate alkalinity of the wash-water, the material was drained off and dried by standing in the air. Analysis gave the following results:

I. 0.2148 gram substance gave 0.0304 gram CO_2, and 0.0762 gram H_2O.

II. 0.2370 gram substance gave 0.0334 gram CO_2, and 0.0854 gram H_2O.

III. 0.2263 gram substance gave 0.09566 gram Al_2O_3, and 0.0400 gram Na_2SO_4.

IV. 0.2137 gram substance gave 0.09116 gram Al_2O_3, and 0.0375 gram Na_2SO_4.

	I.	II.	III.	IV.
CO_2	14.15	14.09	....	....
H_2O	35.47	36.03	....	....
Al_2O_3	....	....	42.27	42.66
Na_2O	....	....	7.72	7.66

Averaging, the composition appears to be:

CO_2	14.12
H_2O	35.75
Al_2O_3	42.47
Na_2O	7.69
	100.03

The 7.69 per cent. of sodium oxide present require 10.91 per cent. of carbon dioxide to form sodium bicarbonate; evidently there is an excess above this quantity of 3.21 per cent.

Here then, as in the case of preparation *B*, the aluminium must assist in holding the carbon dioxide in combination.

Preparation D from Connetable Rock.

At this stage of the investigation it seemed important to carry the washing of the precipitates to the utmost perfection attainable, in the hope of getting a substance which should contain no sodium whatever. The test of complete washing up to this time had been the absence of any effect upon phenol phthaleïn by the cold wash-water decanted from the precipitate. Frequently also the wash-water was evaporated to dryness on the water-bath and, if any residue at all was left, it amounted to so little toward the end of the washing that the rule of boiling to expel carbon dioxide in the phenol-phthaleïn test had not been uniformly observed. From this time on the test consisted in adding a few drops of a solution of phenol phthaleïn, and invariably boiling to expel traces of carbon dioxide; the washing was discontinued only when not the faintest trace of pink color was discernible.

To fulfil this requirement, more washings became necessary but with the result, as will be seen, that the sodium was all but completely removed while the carbon dioxide did not fall below 4 per cent. in any case, and, in three of the four remaining cases, amounted to about 8 per cent.

Preparation *D* was made in the manner already described for *A*, *B*, and *C*. Instead of washing in open cylinders, however, glass-stoppered bottles were used; for some reason the precipitates settled throughout the series of washings more slowly than any of the preceding preparations, passing however, as the others had done, through the specially slow-settling stage. This preparation was washed twenty-four times; many of the settlings required ten hours, and some more than this. After drying in the air, analysis gave the following results:

I. 0.2369 gram substance gave 0.0206 gram CO_2, and 0.1188 gram H_2O.

II. 0.2320 gram substance gave 0.0188 gram CO_2, and 0.1159 gram H_2O.

III. 0.4215 gram substance gave 0.1716 gram Al_2O_3.

IV. 0.2238 gram substance gave 0.0895 gram Al_2O_3.
V. 0.3371 gram substance gave 0.1379 gram Al_2O_3.
VI. 0.2818 gram substance gave 0.0062 gram Na_2SO_4.
VII. 0.2158 gram substance gave 0.0070 gram Na_2SO_4.

	I.	II.	III.	IV.	V.	VI.	VII.
CO_2	8.69	8.10	....	....	....	....	....
H_2O	50.15	49.95	....	....	....	....	....
Al_2O_3	....	....	40.71	40.00	40.91	....	....
Na_2O	....	....	....	....	....	0.96	1.41

Averaging these determinations we have:

CO_2	8.39
H_2O	50.05
Al_2O_3	40.54
Na_2O	1.18
	100.16

The maximum amount of carbon dioxide which the 1.18 per cent. of sodium oxide can combine with is 1.67 per cent; there is present in the compound 6.72 per cent. of carbon dioxide in excess of this amount. This substance appears to be a highly basic carbonate of aluminium aside from the small percentage of sodium oxide found.

Preparation E from Connetable Rock.

This was made in the usual manner. Until the sixth washing the precipitate settled quickly and perfectly; after this it settled very slowly, taking ten days to settle between the eighth and ninth washings. After the ninth washing no alkali could be detected in the wash-water. The material was air-dried and analyzed.

I. 0.2197 gram substance gave 0.0192 gram CO_2, and 0.0928 gram H_2O.

II. 0.2149 gram substance gave 0.0202 gram CO_2, and 0.0910 gram H_2O.

III. 0.2053 gram substance gave 0.1017 gram Al_2O_3.

IV. 0.2039 gram substance gave 0.1023 gram Al_2O_3.

V. 0.2053 gram substance gave NaCl corresponding to 0.000403 gram Cl (volumetrically determined). Strength of $AgNO_3$ solution, 1 cc. = 0.000982 gram Cl.

VI. 0.2039 gram substance gave NaCl corresponding to 0.000689 gram Cl.

	I.	II.	III.	IV.	V.	VI.
CO_2	8.74	9.39	....	....	....	....
H_2O	42.24	42.34	....	....	....	....
Al_2O_3	....	....	49.54	50.17	....	....
Na_2O	....	....	....	....	0.17	0.29

Averaging these figures we have:

CO_2	9.06
H_2O	42.29
Al_2O_3	49.85
Na_2O	0.23
	101.43

Neglecting the small amount of sodium oxide present, this preparation, like the preceding, is a highly basic carbonate of aluminium.

Preparation F from Connetable Rock.

This was made in the same way as the preceding. It was washed and allowed to settle 33 times, when the wash-water no longer had an alkaline reaction. After drying in the air it was analyzed.

I. 0.2333 gram substance gave 0.0177 gram CO_2, and 0.0909 gram H_2O.

II. 0.2053 gram substance gave 0.0155 gram CO_2 and 0.0809 gram H_2O.

III. 0.2075 gram substance gave 0.1103 gram Al_2O_3.

IV. 0.1979 gram substance gave 0.1042 gram Al_2O_3.

V. 0.1680 gram substance gave 0.0893 gram Al_2O_3.

VI. 0.1501 gram substance gave 0.0794 gram Al_2O_3, and 0.0040 gram Na_2SO_4.

	I.	II.	III.	IV.	V.	VI.
CO_2	7.59	7.55	....	....	....	....
H_2O	38.96	39.41	....	....	....	....
Al_2O_3	....	....	53.16	52.65	53.15	52.90
Na_2O	....	....	....	....	....	1.16

Averaging these we have:

CO_2	7.57
H_2O	39.18
Al_2O_3	52.96
Na_2O	1.16
	100.87

Again, in this compound we have the conditions required by a highly basic carbonate of aluminium.

Preparation G from Connetable Rock.

This was prepared, washed, and dried in the same manner as the preceding preparations.

Analysis:

I. 0.2280 gram substance gave 0.0097 gram CO_2, and 0.0796 gram H_2O.

II. 0.2353 gram substance gave 0.0088 gram CO_2, and 0.0822 gram H_2O.

III. 0.1636 gram substance gave 0.0998 gram Al_2O_3, and NaCl corresponding to 0.000638 gram Cl (volumetrically determined).

	I.	II.	III.
CO_2	4.25	3.74	....
H_2O	34.91	34.93	....
Al_2O_3	....	....	61.00
Na_2O	....	....	0.34

Averaging these figures we have:

CO_2	3.99
H_2O	34.92
Al_2O_3	61.00
Na_2O	0.34
	100.25

This compound is not far removed in composition from aluminium hydroxide, $Al_2(OH)_6$.

Summary of Analytical Results Obtained in this Investigation.

	Acid-soluble, commercial alumina, after washing.	A.	B.	C.	D.	E.	F.	G.
CO_2	17.35	24.72	9.06	14.12	8.39	9.06	7.57	3.99
H_2O	22.31	21.74	39.25	35.75	50.05	42.29	39.18	34.92
Al_2O_3	48.88	38.02	49.56	42.47	40.54	49.85	52.96	61.00
Na_2O	12.22	17.38	2.47	7.69	1.18	0.23	1.16	0.34
	100.76	101.86	100.34	100.03	100.16	101.43	100.87	100.25

Summary of Results by Previous Investigators.

	Bley.[1] I.	Bley.[1] II.	Muspratt.[2]	Rose.[3]	Langlois.[4]	Wallace.[5]	Barratt.[6]	Urbain and Renoul.[7]
CO_2	6.14	5.82	8.97	12.91	26.77	7.72	14.26	none	11
H_2O	40.62	46.43	44.22	42.23	23.42	43.48	29.55	34.97	37
Al_2O_3	47.25	47.75	46.82	44.86	34.48	48.80	56.19	65.03	52
$(NH_4)_2O$	....	....	....	....	15.33	....	....	....	..

In view of the results obtained in this investigation, it hardly seems reasonable to continue a denial of the existence of at least a basic carbonate of aluminium.

Furthermore, there seem to be double carbonates of alumina and the alkalies, as indicated by the conduct and the analyses of "commercial alumina after washing," and preparation *A*, from both of which apparently even hot water would not wash out any more alkaline matter. Preparations *B* to *G*, both inclusive, are substances which contain an excess of carbon dioxide well above the maximum amount with which the sodium oxide present is capable of combining.

In the case of preparations *D* to *G*, both inclusive, the amounts of sodium oxide present are very small, so that it must be concluded that these bodies either are, or at least contain, basic carbonate of aluminium. Preparation *G* is but slightly removed in composition from the hydroxide, $Al_2(OH)_6$, and probably longer continued treatment with water would have converted it entirely into the hydroxide. It will be remembered that Barratt found 3 per cent. of carbon dioxide in the preparation analyzed by him; he ascribed it to alkaline carbonate still to be washed out, but it is not improbable that the substance was similar to preparation *G*; he did not ana-

[1] Different analyses of the same preparation showed poor agreement. Methods of analysis are not definitely stated.

[2] Method of analysis not stated. Barratt's work was done under Muspratt's direction, and the latter makes no attempt to explain his previous results, but apparently accepts Barratt's conclusions as final.

[3] No one else found ammonia present when the precipitate was formed by ammonium carbonate.

[4] Water apparently determined by difference.

[5] Wallace did not wash entirely free from alkali and calculated results after subtracting calculated weight of sodium bicarbonate assumed to be present.

[6] Barratt at first found 3 per cent. of CO_2 but, after more washing, obtained $Al_2(OH)_6$. He very probably decomposed a carbonate of aluminium by protracted washing.

[7] Figures given only in round numbers.

lyze it fully but continued washing, ultimately obtaining the hydroxide.

Of considerable interest in this connection is the mineral hovite discovered and analyzed by J. H. and G. Gladstone[1] and described in Dana's Mineralogy, p. 709.

The following are analyses of the mineral collyrite, associated with which hovite occurs; the samples include hovite:

	SO_2.	CO_2.	Al_2O_3.	CaO.	H_2O.
I.	6.22	10.91	41.04	7.37	33.16 = 98.70
II.	5.87	14.77	39.58	11.22	28.56
III.	5.41	18.15	36.32	11.62	29.16
IV.	5.30	14.14	40.51	9.18	30.87

In I. the 7.37 per cent. calcium oxide present require 11.6 per cent. of carbon dioxide to form calcium bicarbonate; this is only slightly in excess of the amount actually present.

II. requires 17.6 per cent. of carbon dioxide to form bicarbonate of calcium, III. 18.26, and IV. 14.4 per cent.

The following is quoted from Dana's Mineralogy: "J. H. and G. Gladstone state that there is carbonic acid enough in the collyrite to form a bicarbonate with the lime present; but this view of the composition is set aside because of the solubility of the so-called bicarbonate, and its being unknown in the solid state; and hence they suggest that the excess of carbonic acid may be combined in the mineral with alumina, making a hydrous carbonate of alumina and lime, or perhaps replaces part of the silica in the alumina silicate.

"But although the bicarbonate referred to is known only in solution, the most likely condition for finding it in the mineral kingdom is in one of the hydrous silicates of alumina, like collyrite, in which there is present much water, loosely held; the mineral therefore is most probably a carbonate of the formula above given; especially since *a carbonate in which Al_2O_3 or Fe_2O_3 enters is, as the authors admit, yet unknown to chemistry.*"[2]

In view of the facts developed in the present investigation, it seems highly probable that the mineral, instead of being a bicarbonate, is really a basic double carbonate of aluminium and calcium.

[1] Phil. Mag., IV., **23**, 462, 1862.

[2] The italics are mine.—W. C. D.

In carrying out this investigation I have had the assistance of three of my pupils, Miss Altha T. Coons, Mr. Clarence B. Hoadley, and Mr. Reuben G. Bennett. The work has presented a number of tedious and trying features, and I feel much indebted to my assistants for the unflagging zeal which they have shown throughout.

SWARTHMORE COLLEGE, PA.,
May 25, 1897.

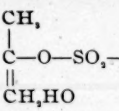
ALIPHATIC SULPHONIC ACIDS.

I.—(1, 2)-ETHANEDISULPHONIC ACID.

BY ELMER P. KOHLER.

The work described in this paper is the result of an effort to find general methods for the preparation of unsaturated aliphatic sulphonic acids, and particularly of isomeric sulphonic acids analogous to fumaric and maleïc acids.

Only two unsaturated sulphonic acids have hitherto been described. The first was obtained by Schrohe,[1] by passing allylene into sulphuric acid and boiling the product with water. The product was isolated and analyzed in the form of the barium salt, and was not further studied. According to later work by Orndorff and Young[2] the acid is not an unsaturated sulphonic acid but probably isopropenylsulphuric acid,



The second was prepared by Rad[3] by boiling allyl iodide with potassium sulphite. It was isolated, only in the form of complex double salts from which it was impossible to obtain either the free acid or any simple derivatives of it. I have found that unsaturated sulphonic acids can be prepared by a number of the methods available for the preparation of unsaturated compounds. All of these methods, however, meet with the difficulties encountered by Rad; either the unsaturated sulphonic acid is destroyed almost as fast as formed, or

[1] Ber. d. chem. Ges., **18**, 18 and 367. [2] This JOURNAL, **15**, 273.
[3] Ann. Chem. (Liebig), **161**, 218.

it is obtained in the form of double salts from which it is difficult, or impossible, to isolate the free acid. Thus every effort to realize the reaction represented by the equation

$$\begin{matrix} CH_2OH \\ | \\ CH_2SO_3H \end{matrix} - H_2O = \begin{matrix} CH_2 \\ \| \\ CHSO_3H, \end{matrix}$$

resulted in a complete decomposition of the sulphonic acid. It is comparatively easy, on the other hand, to split off hydrobromic acid from (1, 2)-bromsulphonic acids. The product, however, is always one or more double salts. From (1, 2)-monobromethanesulphonic acid, for example, a double salt of ethylenesulphonic acid is obtained according to the reaction:

$$\begin{matrix} CH_2Br \\ | \\ 2CH_2SO_3K \end{matrix} + 2KOC_2H_5 = \left(\begin{matrix} CH_2 \\ \| \\ CH_2SO_3K \end{matrix} \right)_2 KBr + KBr + 2C_2H_5OH.$$

The result is the same when Strecker's reaction is applied to the halogen substitution-products of unsaturated hydrocarbons. Thus monobromethylene gives, with potassium sulphite, the same salt that was obtained from (1, 2)-monobromethanesulphonic acid,

$$2CH_2{=}CHBr + 2K_2SO_3 = (CH_2{=}CHSO_3K)_2KBr + KBr.$$

These double salts are extremely stable; they can be boiled with lead acetate for days without complete precipitation of all the halogen present. They are readily decomposed by warming with concentrated sulphuric acid, but under these conditions they also readily take up water and pass into saturated oxysulphonic acids:

$$2(CH_2{=}CHSO_3K)_2KBr + 4H_2O + 3H_2SO_4 = 4CH_2OHCH_2SO_3H + 3K_2SO_4 + 2HBr.$$

The result, therefore, is a mixture of sulphonic acids, which it is extremely difficult to separate. In the case of unsaturated disulphonic acids, of the fumaric acid type, Strecker's reaction fails altogether, since the dihalogen addition-products of the acetylene hydrocarbons do not react with sulphites.

No better results are obtained by direct reaction between acetylene hydrocarbons and sulphuric acid. Acetylene hydro-

carbons are readily absorbed by sulphuric acid and, after warming, the solution always contains some unsaturated sulphonic acid. These unsaturated acids are so easily oxidized, however, that the yield of pure acid ultimately obtained is always small. The unsatisfactory yield obtained by all the methods described above, led to an attempt to prepare unsaturated sulphonic acids by splitting off sulphur dioxide from saturated polysulphonic acids. It has frequently been observed that unsaturated acids and alcohols combine directly with acid sulphites, to form saturated sulphonic acids. Thus, sulphosuccinic acid was obtained by Credner[1] by direct addition of acid sulphites to fumaric acid, and by Messel[2] by the addition of the same substance to maleïc acid. It seemed probable, therefore, that under suitable conditions, sulphurous acid could be split off from sulphonic acids. This, in the case of polysulphonic acids, ought to give unsaturated sulphonic acids. I selected (1, 2)-ethanedisulphonic acid for study, because it is readily obtained in quantity. I found that the diacid chloride of this substance loses sulphur dioxide and hydrochloric acid with the greatest ease, and passes into an unsaturated sulphonic acid. Thus by simply boiling the chloride with water the greater part of it is converted into ethylenesulphonic acid—the lowest member of the unsaturated aliphatic sulphonic acids—according to the equation :

$$\begin{matrix} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{matrix} + H_2O = \begin{matrix} CH_2 \\ \| \\ CH_2SO_2OH \end{matrix} + 2HCl + SO_2.$$

To determine to what extent this reaction can be used for the preparation of unsaturated sulphonic acids, twenty-three sulphonic acids were studied with reference to their behavior towards phosphorus pentachloride, and with reference to the behavior of the resulting chloride towards water. The general results—to which there are no exceptions in the case of the acids studied—were as follows :

1. Monosulphonic acids and (1, 1)-chlor- or brommonosubstitution-products of monosulphonic acids react readily with phosphorus pentachloride in the cold. The product is a nor-

[1] Ztschr. Chem. [2], **6**, 77.
[2] *Ibid*, [2], **6**, 459; and Ann. Chem. (Liebig), **157**, 15.

mal sulphone chloride, which, when decomposed with water, passes back into the acid :

(1) $C_2H_5SO_3K + PCl_5 = C_2H_5SO_2Cl + POCl_3 + KCl.$
(2) $C_2H_5SO_2Cl + H_2O = C_2H_5SO_3OH + HCl.$
(3) $CH_3.CHBrSO_3K + PCl_5 = CH_3CHBrSO_2Cl + POCl_3 + KCl.$
(4) $CH_3CHBrSO_2Cl + H_2O = CH_3CHBrSO_3H + HCl.$

2. (1, 2)-Chlorsulphonic acids, and (1, 2)-bromsulphonic acids likewise react with phosphorus pentachloride in the cold. When the sulphone chloride thus obtained is boiled with water, two reactions take place. Most of the chloride passes back into the acid. A small quantity of the chloride, however, reacts so as to form an unsaturated sulphonic acid :

$$CH_2BrCH_2SO_2Cl + H_2O = CH_2{=}CHSO_3H + HCl + HBr.$$

3. (1, 1)-Disulphonic acids do not react with phosphorus pentachloride in the cold. The product, on heating, is mainly a (1, 1)-chlorsulphone chloride,

$$CH_2(SO_3K)_2 + 2PCl_5 = CH_2ClSO_2Cl + 2POCl_3 + 2KCl + SO_2.$$

Other chlorine substitution-products are, however, generally formed at the same time. Thus, (1, 1)-ethanedisulphonic acid gives (1, 1)-chlorethanesulphone chloride, (2)-chlor-(1, 1)-chlorethanesulphone chloride, and (1, 1)-dichlorethane.

4. (1, 2)-Disulphonic acids do not react with phosphorus pentachloride in the cold. On heating, a disulphone chloride is formed which reacts with water in two different ways. The main reaction always results in the formation of an unsaturated sulphonic acid :

$$\begin{matrix} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{matrix} + H_2O = \begin{matrix} CH_2 \\ \| \\ CH_2SO_3H \end{matrix} + 2HCl + SO_2.$$

A minor reaction regenerates the acid.

5. (1, 1)-Sulphocarbonic acids and (1, 2)-sulphocarbonic acids slowly react with phosphorus pentachloride in the cold. The product is always a chlorine substitution-product of a diacid chloride. The reaction of this product with water is generally complicated, and appears to be different in different

cases. Among the products there is always an unsaturated sulphonic acid.

These results, which will be treated in detail in subsequent papers, show that whenever an unsaturated acid is formed by the decomposition of a chloride of a saturated acid, with water, two reactions take place side by side; the one resulting in the regeneration of the saturated acid, the other in the formation of an unsaturated acid. To determine what conditions are most favorable to the one or the other of these reactions I studied the behavior of (1, 2)-ethanedisulphone chloride towards a number of different reagents, and under a variety of different conditions. The results obtained form the special subject of this paper.

(1, 2)-Ethanedisulphonic Acid.

(1, 2)-Ethanedisulphonic acid was first obtained by Buckton and Hofmann[1] by the action of fuming sulphuric acid on propionitrile. These investigators studied only the free acid and a few of its salts. Some years later Königs[2] prepared the chloride by treating the sodium salt with phosphorus pentachloride. He assigned to it the symmetrical formula

$$\begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl, \end{array}$$

and showed that by the action of phosphorus pentachloride the two sulphonic acid residues can be successively replaced by chlorine. Königs also observed that when the alcoholic solution of the chloride is boiled sulphur dioxide is evolved. More recently, Otto[3] and Casanova reduced the chloride with zinc dust and water, and obtained the corresponding sulphinic acid. Beyond this nothing is known either of the acid or of its derivatives.

I. Preparation of Materials.

1. Sodium Ethanedisulphonate.—The sodium salt of (1, 2)-ethanedisulphonic acid is readily prepared by boiling ethylene bromide with sodium sulphite in concentrated aqueous solu-

[1] J. Chem. Soc., 9, 250. [2] Ber. d. chem. Ges., 7, 1163.
[3] J. prakt. Chem., [2] 36, 439.

tion and recrystallizing the product from water. It is considerably less soluble than sodium bromide and forms no double salts, hence Beilstein's modification of Strecker's reaction offers no advantages. The yield is almost quantitative if the sulphite is used in sufficient excess and the solution kept concentrated. In more dilute solutions only one of the bromine atoms of ethylene bromide is replaced, and sodium monobromethanesulphonate is obtained. This is slowly decomposed by boiling water with formation of sodium isethionate:

$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} + Na_2SO_3 = \begin{matrix}CH_2Br\\|\\CH_2SO_3Na\end{matrix} + NaBr.$$

$$\begin{matrix}CH_2Br\\|\\CH_2SO_3Na\end{matrix} + H_2O = \begin{matrix}CH_2OH\\|\\CH_2SO_3Na\end{matrix} + HBr.$$

The hydrobromic acid liberated then reacts with some of the sulphite present, which accounts for the evolution of sulphur dioxide observed by James.[1] To avoid this secondary reaction the following method of procedure was adopted: Two liters of water, in a three-liter flask supplied with inverted condenser and dropping-funnel, were saturated with sodium sulphite at the boiling-point, and ethylene bromide added through the funnel (as fast as it went into solution) until the odor of sulphur dioxide became perceptible at the mouth of the condenser. The solution was then allowed to cool, when most of the sulphonate formed crystallized out in a practically pure state. After filtration the liquid was heated to boiling, again saturated with sodium sulphite, and ethylene bromide introduced as before. By a repetition of this process about 500 grams of the sulphonate can be obtained from the same liquid, before sodium bromide begins to separate out with the sulphonate. In a trial experiment, 450 grams of ethylene bromide and 1300 grams of sodium sulphite gave 420 grams of pure anhydrous sodium salt—about 95 per cent. of the theoretical yield.

2. *Preparation of the Acid.*—Since the free acid cannot be obtained by decomposing the sulphone chloride the easiest

[1] J. Chem. Soc., 43, 44.

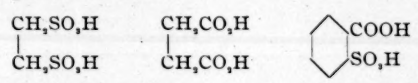
way to obtain it, in quantity, is to oxidize ethylene sulphocyanate. This is easily obtained from ethylene bromide by following the directions of Glutz.[1] A much better way of purifying it, however, is to recrystallize it from 1 : 3 nitric acid. After one recrystallization it is obtained in colorless orthorhombic pyramids, which melt sharply at 91° C. If the pure ethylene sulphocyanate thus obtained is warmed with ordinary concentrated nitric acid until vigorous oxidation commences, and the reaction is then allowed to proceed without further heating until gas is no longer evolved, the product, on evaporation, is pure ammonium ethanedisulphonate. If the sulphocyanate is boiled with fuming nitric acid, the product is the free acid. To prepare the latter in a pure condition the sulphocyanate was boiled with fuming nitric acid until a small quantity of the liquid no longer solidified on evaporation, The resulting liquid was diluted with a little water and evaporated to small volume on the water-bath. A dark viscid mass was thus obtained, which solidified almost completely when kept over sulphuric acid for several days. The crystals, when rapidly separated from the liquid, gave reactions for sulphuric and nitric acids. They were therefore dissolved in boiling glacial acetic acid, to which a small quantity of acetic anhydride had been added. This solution, on standing, almost solidified with a mass of slender needles, which melted sharply at 100°. An analysis showed that the substance is pure anhydrous ethanedisulphonic acid :

	Calculated for $C_2H_4S_2O_6$.	Found.
C	12.63	12.5
H	3.2	3.3

3. Preparation of the Chloride from the Sodium Salt.—In accordance with the rule given above, the sodium salt of (1, 2)-ethanedisulphonic acid does not react with phosphorus pentachloride in the cold. Even at the temperature of boiling water the reaction is started with difficulty, while above this temperature phosphorus pentachloride readily replaces one of the sulphonic acid groups with chlorine. To prepare large quantities of the chloride the method of procedure was as fol-

[1] Ann. Chem. (Liebig), 143, 313

lows: The sodium salt, dried at 140° and ground to a fine powder, was intimately mixed with a slight excess above the calculated quantity of the pentachloride, and a small quantity of this mixture introduced into a flask and heated over the free flame until reaction commenced; the flask was then transferred to a water-bath, and the rest of the mixture added as fast as liquefaction took place. As soon as the reaction was complete the liquid was poured into a large evaporating dish, and most of the phosphorus oxychloride removed by evaporation on the water-bath. The pasty residue was then allowed to cool, and gradually ground up with ice-water. It was thus obtained as a fine white powder which, after drying on plates, was almost pure, containing only small quantities of unchanged salt and sodium chloride. To get a perfectly pure product it is best to recrystallize from chloroform or carbon tetrachloride with the help of a Soxhlet extraction-apparatus. All the chloride used in the following experiments was purified in this way. From chloroform it crystallizes in large, compact, orthorhombic tables, which melt at 91° C. In a trial experiment 200 grams of sodium salt gave 180 grams of pure chloride instead of 193 grams calculated. The good yield obtained shows that under these conditions but one chloride is formed, while from the close analogy in structure, between (1, 2)-ethanedisulphonic acid, succinic acid, and orthosulphobenzoic acid:



it seemed probable that the former, like the two latter, would, under suitable conditions, form both a symmetrical and an unsymmetrical chloride:

To study the influence of temperature the sodium salt was first ground up with phosphorus oxychloride and the penta-

chloride then added in small portions. Reaction took place in the cold, and the flask was kept in ice-water until the reaction was completed. The solution of the chloride in phosphorus oxychloride was filtered off, and the oxychloride removed at the ordinary temperature, by drawing a rapid current of dry air through it. The same chloride crystallized out. Twenty grams of the sodium salt gave 18.5 grams of pure chloride. The same result was obtained when carbon tetrachloride and carbon bisulphide were used as solvents for the pentachloride.

4. Preparation of the Chloride from the Acid and Carbonyl Chloride.—The free acid behaves towards phosphorus pentachloride exactly like the sodium salt; the chloride melting at 91° C. is obtained in theoretical quantity. To avoid the use of chloride of phosphorus one molecule of the acid was sealed up with slightly more than two molecules of carbonyl chloride in toluene solution, and the two allowed to remain in contact, at the ordinary temperature, until all the acid had gone into solution. The tube, when opened, showed considerable pressure, which was found to be due to carbon dioxide. The contents were allowed to evaporate spontaneously in the air, when the pure chloride, melting at 95°, crystallized out. The reaction is quantitative—20 grams of the acid gave 22.5 grams of the chloride. The only reaction which seems possible under these conditions is represented by the equation:

$$\begin{matrix}CH_2SO_3OH\\|\\CH_2SO_3OH\end{matrix} + 2COCl_2 = \begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + 2CO_2 + 2HCl.$$

Hence (1,2)-ethanesulphone chloride must be regarded as symmetrical. As unsymmetrical chlorides are generally obtained through the anhydrides, many unsuccessful efforts were made to obtain an anhydride of the disulphonic acid. The acid loses one of the sulphonic acid residues more readily than it loses a molecule of water.

Chemical Properties of the Chloride.

1. Behavior on Heating.—Heated in quantity in an oil-bath, the chloride begins to sublime perceptibly at about 80°, then melts to a clear colorless liquid at 91°. If the chloride is perfectly pure this liquid can be heated to 150° without a trace of

decomposition. At this temperature the chloride sublimes rapidly, the vapor condensing in the form of long slender needles, with the same melting-point as before. At 160° a slow evolution of gas is observed, and if the temperature is kept constant between 160° and 165°, a colorless liquid slowly distils over, while the residue becomes darker in color. The distillation stops when the weight of the distillate is about one-fourth of the original weight of chloride. The gas evolved was found to be sulphur dioxide with a trace of hydrochloric acid. The distillate was submitted to fractional distillation, but it was found impossible to get any fraction boiling at a constant temperature. Hence, all the fractions were combined, and the whole distillate boiled with water in a flask connected with an inverted condenser. Most of it went into solution with evolution of hydrochloric acid. The portion insoluble in water was distilled off with steam. It was found to be a mixture containing carbon, hydrogen, and chlorine, but no sulphur, and it was not further studied. The aqueous solution remaining after distillation with steam was evaporated on the water-bath until free from hydrochloric acid, then neutralized with ammonia, and the product purified by recrystallization from absolute alcohol. Thus purified it was obtained in the form of large, colorless needles, or plates, readily soluble in alcohol and water, and melting at 192°. An analysis of the substance, dried at 120°, gave the following results :

	Calculated for $C_2H_8ClSO_3N$.	Found. I.	II.
C	14.0	14.8	14.7
H	5.1	5.2	5.25
Cl	22.0	22.2	22.18
N	8.73	8.4	8.8

The substance analyzed was the ammonium salt of (1, 2)-chlorethanesulphonic acid. It was compared with a specimen of this salt, obtained by treating isethionic acid with phosphorus pentachloride, and converting the resulting (1, 2)-chlorethanesulphone chloride into the ammonium salt. The two were found identical. A mixture of the two melts sharply at the same temperature at which each melts singly. The

distillate, therefore, was composed principally of (1, 2)-chlorethanesulphone chloride.

The residue, after heating, was a tarry mass, which contained both chlorine and sulphur, but no pure substance could be isolated from this. When the chloride is heated, therefore, about 25 per cent. of it is decomposed according to the equation:

$$C_2H_4(SO_2Cl)_2 = CH_2Cl.CH_2SO_2Cl + SO_2.$$

The rest suffers a more complex decomposition, resulting in the formation of halogen substitution-products of the hydrocarbons along with more complicated products.

2. Action of Water.—The chloride reacts with water at all temperatures; both sulphur dioxide and hydrochloric acid can be detected in ice-water that has stood in contact with it for a few minutes. At ordinary temperatures the reaction proceeds very slowly. To follow the reaction quantitatively five portions of one gram each were sealed up with quantities of water varying from 1 to 10 grams, and set aside. The portion which had been sealed up with but one gram of water had not decomposed completely, when the tube was opened, after a lapse of two years. All the remaining portions required from three to four months for complete solution. Two of the tubes were opened under water previously freed from air, and the amount of sulphur dioxide determined by distillation into standard iodine.

I. The sulphur dioxide from one gram of chloride, sealed up with 3 grams of water, reduced 119.3 cc. standard iodine, and, therefore, contained 0.235 gram sulphur dioxide, which is equivalent to 23.5 per cent. of the weight of chloride taken.

II. The sulphur dioxide from one gram chloride sealed up with 10 grams water reduced 116.7 cc. of standard iodine. It, hence, contained 0.23 gram sulphur dioxide, equivalent to 23 per cent. of the weight of chloride.

The two remaining tubes were opened under strongly acid silver nitrate solution, and the hydrochloric acid determined gravimetrically:

III. One gram chloride gave 1.2660 gram silver chloride containing 0.3140 gram chlorine, which is equivalent to 31.4 per cent. of the chloride taken.

IV. One gram chloride gave 1.2640 gram silver chloride containing 0.3134 gram chlorine, equivalent to 31.34 per cent. Calculated for ethanesulphone chloride, 31.27 per cent. chlorine, and 56 per cent. sulphur dioxide.

These results show that when the chloride reacts with cold water all of the chlorine is obtained as hydrochloric acid, while somewhat less than half (41.2 per cent.) of the sulphur is split off as sulphur dioxide.

Boiling water decomposes the chloride much more readily, a steady stream of sulphur dioxide being given off. To isolate the organic products, the resulting liquid was boiled until all the sulphur dioxide had been expelled when evaporated until a few drops of the residue no longer gave a precipitate with silver nitrate. The thick, straw-colored liquid thus obtained was neutralized with an excess of concentrated ammonia, and evaporated to complete dryness. To remove the last traces of water, small quantities of absolute alcohol were added and the evaporation repeated until finally the entire product was obtained in the form of a yellowish powder. This was transferred to a flask connected with an inverted condenser, and boiled with absolute alcohol. Most of the powder dissolved. The residue insoluble in alcohol was easily purified by solution in a small quantity of water and precipitation with alcohol. An analysis of the substance dried at 120° gave the following result:

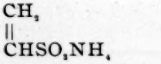
	Calculated for $C_4H_{12}S_2O_4N_2$.	Found. I.	II.
C	10.8	10.46	11.0
H	5.4	5.38	5.45
N	12.5	12.5	12.6

The substance was compared with the ammonium salt of (1, 2)-ethanedisulphonic acid obtained by boiling ethylene bromide with ammonium sulphite, and the two were found the same. 50 grams of the chloride gave 4.2 grams of this salt corresponding to 8.4 per cent, of the chloride. The alcoholic solution, on evaporation, deposited a second ammonium salt, which was purified by several recrystallizations from absolute alcohol. Analysis showed that the substance had the composition of an ammonium salt of ethylenesulphonic acid:

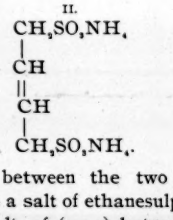
	Calculated for $C_3H_7SO_3N$.	Found. I.	II.
C	19.2	19.05	19.1
H	5.64	5.84	5.4
N	11.2	11.2	11.22
S	25.5	25.5	25.4

The salt is extremely soluble in water, readily soluble in 95 per cent. alcohol, moderately soluble in absolute alcohol, insoluble in ether. It cannot be crystallized from water. From absolute alcohol it crystallizes in large, thin plates, and from ordinary alcohol in monoclinic tables. Heated rapidly, it melts almost completely at 156°, but solidifies again a few degrees above this point. Like the free acid and all the other salts it instantly reduces alkaline permanganate solution, and reacts with chlorine, bromine, the halogen acids, etc., in the cold. These reactions show that it is a salt of an unsaturated acid. The method of preparation and the analyses permit of but two possibilities :

I.



II.



The simplest way to decide between the two is by reduction. The former should give a salt of ethanesulphonic acid, the latter the corresponding salt of (1, 4)-butanedisulphonic acid—both well-known substances. Experiments in this direction, showed, however, that like allyl alcohol and some unsaturated carbonic acids the substance is reduced with great difficulty. A concentrated aqueous solution of the ammonium salt was therefore treated with slightly more than one molecule of acid ammonium sulphite, the solution boiled for a few hours, and allowed to evaporate spontaneously in the air. The characteristic monoclinic prisms of the diammonium salt of (1,2)-ethanedisulphonic acid crystallized out. This could only be formed from a substance having formula I :

$$\begin{array}{l}CH_2\\ \|\\ CHSO_3NH_4\end{array} + \begin{array}{l}SO_3NH_4\\ |\\ H\end{array} = \begin{array}{l}CH_2SO_3NH_4\\ |\\ CH_2SO_3NH_4.\end{array}$$

50 grams of the chloride gave 24 grams of the ammonium salt, equivalent to 90 per cent. of the chloride.

Since the analyses showed that the liquid obtained by the action of water on the chloride, contains all the chlorine in the form of hydrochloric acid and nearly one-half of the sulphur in the form of sulphur dioxide, the ethylenesulphonic acid must have been formed in one of two ways: either the chloride simultaneously loses sulphur dioxide and hydrochloric acid and thus passes directly into the unsaturated acid according to the equation:

$$C_2H_4(SO_2Cl)_2 + H_2O = C_2H_3SO_3H + SO_2 + HCl;$$

or else one of the sulphonic acid groups is first replaced by hydroxyl, and the resulting isethionic acid then loses water during the process of concentrating the acid solution:

$$\text{I.}\quad \begin{array}{l}CH_2SO_2Cl\\ |\\ CH_2SO_2Cl\end{array} + 2H_2O = \begin{array}{l}CH_2OH\\ |\\ CH_2SO_3H\end{array} + SO_2 + 2HCl.$$

$$\text{II.}\quad \begin{array}{l}CH_2OH\\ |\\ CH_2SO_3H\end{array} - H_2O = \begin{array}{l}CH_2\\ \|\\ CHSO_3H.\end{array}$$

To determine which of these reactions is true 50 grams of the chloride were decomposed with water, and the product immediately neutralized with lead carbonate. After cooling, the precipitated lead salts were removed by filtration, the lead in solution precipitated with hydrogen sulphide, and the solution of the free acid thus obtained neutralized with ammonia. 50 grams of the chloride gave 23.2 grams of the ammonium salt of the unsaturated acid.

The experiments show that when (1,2)-ethanesulphone chloride is decomposed with hot or cold water about 90 per cent, of it reacts according to the equation:

$$\begin{array}{l}CH_2SO_2Cl\\ |\\ CH_2SO_2Cl\end{array} + H_2O = \begin{array}{l}CH_2\\ \|\\ CHSO_3H\end{array} + SO_2 + 2HCl,$$

while only about 10 per cent. reacts according to the equation:

$$C_2H_4(SO_2Cl)_2 + 2H_2O = C_2H_4(SO_2H)_2 + 2HCl.$$

The quantitative course of the reaction can readily be followed by titrating the sulphur dioxide evolved, with standard iodine.

Many experiments, made with a view of determining the conditions which favor the formation of the unsaturated acid, all led to the conclusion that the action is practically independent of external conditions. It varies only within very narrow limits, and then quite irregularly. The maximum percentage of sulphur dioxide obtained was 25.2; the minimum 20.8.

Many transformations of the unsaturated acid have been studied, but for the sake of clearness they will be published in a separate paper.

3. *Action of Alcohol.*—The chlorides dissolve in considerable quantity in cold absolute alcohol. If cold water is added to this solution the chloride is precipitated unchanged. If the solution is allowed to stand, the odor of sulphur dioxide soon becomes perceptible and, after standing for a week, water no longer gives any precipitate. Cold alcohol, therefore, decomposes the chloride much more readily than cold water. The products are easily isolated by distilling off the alcohol, and treating the residue as in previous experiments. The products were found to be the same as those obtained by decomposing the chloride with water, but in quite different quantities:

50 grams of chloride decomposed with cold alcohol gave only 12.2 grams of ammonium ethylenemonosulphonate, corresponding to 45 per cent. of the chloride.

50 grams of chloride, decomposed with boiling alcohol, gave 20 grams of the same salt, corresponding to 60 per cent. of the chloride.

The alcoholic distillate, neutralized with solid soda and submitted to fractional distillation, gave a low-boiling fraction which contained ether, easily recognizable by the odor, and some halogen compound recognized by Beilstein's test. It was heated with an excess of ammonium sulphite in a sealed tube and the product isolated in the usual way. A

nitrogen determination showed that ammonium ethanesulphonate had been formed: Found N, 10.92 per cent; calculated for $C_2H_5NSO_3$, N, 11.1 per cent.

The products of the reaction between alcohol and the chloride are therefore $\begin{matrix}CH_2SO_3H\\|\\CH_2SO_3H\end{matrix}$, $\begin{matrix}CH_2\\\|\\CHSO_3H\end{matrix}$, $(C_2H_5)_2O$, and C_2H_5Cl. Ethyl chloride is probably a secondary product. The main reactions are:

$$(1)\quad \begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + 4C_2H_5OH = \begin{matrix}CH_2SO_3H\\|\\CH_2SO_3H\end{matrix} + 2(C_2H_5)O + 2HCl.$$

$$(2)\quad \begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + 2C_2H_5OH = \begin{matrix}CH_2\\\|\\CHSO_3H\end{matrix} + (C_2H_5)_2O + 2HCl + SO_2.$$

Methyl, propyl, and amyl alcohols react in the same way as ordinary alcohol, but the relative quantities of the two sulphonic acids formed, vary with the different alcohols. Since the presence of the alcohols interferes with the determination of the amount of sulphur dioxide evolved, another method was adopted for following the reaction. In the presence of sodium carbonate, potassium permanganate oxidizes the unsaturated sulphonic acid to sulphuric acid, carbon dioxide, and water. The reaction is quantitative, hence by using standard permanganate the amount of unsaturated acid formed can readily be determined. One-gram portions of the chloride were lowered into a large excess of the boiling alcohol contained in a flask connected with an inverted condenser. After boiling for an hour most of the alcohol was distilled off, the residue neutralized with aqueous sodium carbonate, and the rest of the alcohol completely removed by distillation with steam. The liquid was then cooled and titrated against permanganate, which had been standardized with the sodium salt of the unsaturated acid. The results, expressed in percentages of chloride, are as follows:

	I.	II.	III.	Mean.
Boiling water	88.5	88.0	88.0	88.2
Methyl alcohol	73.0	73.8	73.2	73.3
Ethyl alcohol	60.0	62.0	61.6	61.2
Propyl alcohol	56.8	56.4	56.0	56.4
Amyl alcohol	50.6	50.6	52.0	51.4

As will be seen, the amount of unsaturated acid formed diminishes as the molecular weight of the alcohol increases. This is probably due to the fact that the reaction goes on more slowly in an alcohol of high molecular weight than in an alcohol of low molecular weight. It is independent of the temperature, since the second column of figures was obtained by boiling under an increased pressure of about one atmosphere, the third under diminished pressure.

4. Action of Acids and Alkalies.—Glacial acetic acid readily dissolves the chloride; the resulting solution can be boiled for hours without a trace of decomposition. If water is added to the solution, however, decomposition at once sets in, accompanied by evolution of sulphur dioxide. The reaction can be closely followed by the permanganate method, hence it furnishes an easy method for studying the influence of the mass of water, under strictly comparable conditions. The results showed that the course of the decomposition is entirely independent of the relative amounts of chloride and water. Of the two reactions which invariable take place when the chloride is decomposed with water one requires only one-half as much water as the other, but the result was the same whether the water was used in sufficient quantity for the one or in an excess for the other. The minimum amount of chloride transformed into the unsaturated acid was 82 per cent.; the maximum amount was 86 per cent. With aqueous alkalies the general result is the same—the two reactions take place side by side regardless of the nature or concentration of the alkali.

5. Action of Ammonia.—The amide of ethanedisulphonic acid cannot be prepared from the chloride. The products that are invariably obtained when the chloride and ammonia are brought together are ammonium chloride, ammonium sulphite, ammonium ethanedisulphonate, and anhydrotaurine.

These substances are obtained when dry ammonia gas slowly reacts with the dry chloride; when the two are brought together in the presence of water or in solution in ether, alcohol, benzene, or chloroform; and when dry ammonium carbonate is ground up with the dry chloride. The reaction takes place most smoothly in absolute alcoholic solution. When ammonia is passed into an alcoholic solution of the chloride, kept cool with running water, a dense white precipitate immediately begins to form. If this is rapidly filtered off as soon as the reaction is complete, it is entirely free from organic matter and contains only ammonium chloride and ammonium sulphite. On warming the filtrate, ammonium ethanedisulphonate begins to crystallize out mixed with a small quantity of ammonium chloride. It is best to evaporate the liquid to half its volume and then allow it to cool when almost all of the ammonium salts crystallize out. The remainder of the alcohol is then distilled off, the pasty residue diluted with water, and all of the halogen present precipitated by boiling with silver carbonate. The filtrate from this precipitate contains all the anhydrotaurine along with a small quantity of the ammonium salt. To separate the two the solution is evaporated to small volume, and four times the volume of absolute alcohol added. The ammonium salt remains in solution while the anhydro compound is precipitated as an oil. It is extremely difficult to get this substance sufficiently pure for analysis. It separates out of its aqueous solution as a thick oil, which ultimately solidifies to a gelatinous mass without a trace of crystallization. A small quantity was finally obtained in crystalline form by allowing a dilute glacial acetic acid solution to evaporate slowly over potassium hydroxide. Thus prepared, it consisted of small colorless needles, moderately soluble in water, difficultly soluble in glacial acetic acid, insoluble in alcohol and ether. It melts sharply at 88°.

	Calculated for $C_2H_3NSO_3$.	Found. I.	II.
C	24.7	24.5	24.6
H	4.1	4.3	4.28
N	14.4	14.3	14.3
S	35.0	35.1	35.15

The same substance had previously been obtained, in impure condition, by James,[1] by the action of ammonia upon (1, 2)-chlorethanesulphone chloride:

$$\begin{matrix}CH_2Cl\\|\\CH_2OO_2Cl\end{matrix} + NH_3 = \begin{matrix}CH_2\\|\\CH_2SO_2\end{matrix}>NH + 2HCl.$$

James gives a different melting-point, but a repetition of his experiment showed that the same substance is formed. The main reaction between ethanedisulphone chloride and ammonia must, therefore, be represented by the equation:

$$\begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + NH_3 = \begin{matrix}CH_2\\|\\CH_2SO_2\end{matrix}>NH + 2HCl + SO_2.$$

6. Action of Aniline.—When one molecule of the chloride, dissolved in anhydrous ether, is treated with 4 molecules of aniline a reaction takes place in the cold, sulphur dioxide is given off, and the solution almost solidifies with the aniline salts which separate out. After these salts are filtered off the ether still contains two substances in solution. These are most easily separated by repeated extraction with dilute hydrochloric acid. After extraction the ethereal solution is allowed to evaporate spontaneously, when large monoclinic plates separate out. These were dissolved in alcohol, the solution decolorized with bone-black, and evaporated to crystallization. The substance now crystallized out in thick tables melting at 69°. An analysis gave the following results:

	Calculated for $C_8H_9NSO_2$.	Found. I.	II.
C	52.46	52.3	52.2
H	4.9	4.9	5.1
N	7.65	7.6	7.6
S	17.49	17.55	17.6

The substance is anhydrophenyltaurine,

$$\begin{matrix}CH_2\\|\\CH_2SO_2\end{matrix}>N.C_6H_5,$$

agreeing, in every respect, with the substance obtained by Leymann[2] as one of the products of the action of aniline on

[1] J. prakt. Chem., [2] 20, 383. [2] Ber. d. chem. Ges., 18, 869.

(1, 2)-chlorethanesulphone chloride. From the hydrochloric acid extract a second substance separates out in long needles. This was purified by recrystallization from alcohol containing a small quantity of hydrochloric acid. So purified it forms long colorless needles, which soon become opaque in the air and finally change to a black resinous mass. It is extremely soluble in water, moderately soluble in alcohol, insoluble in ether, and melts at 171°.

	Calculated for $C_{14}H_{17}N_2SO_2Cl$.	Found. I.	II.
C	53.8	53.6	53.5
H	5.44	5.64	5.5
S	10.24	10.24	10.4
Cl	11.4	11.5	11.5
N	8.5	8.5	8.5

The substance is the hydrochloric acid salt of anilidoethanesulphone anilide,

$$\begin{array}{l} HCl.HN.C_6H_5 \\ | \\ CH_2.CH_2SO_2NHC_6H_5. \end{array}$$

By decomposing the salt with the calculated quantity of an alkali, the free base is obtained as an oil, which is difficult to obtain in crystalline form. It is insoluble in water but, by reason of the two differently located aniline residues, soluble both in alkalies and acids. If ammonium chloride solution is allowed to diffuse slowly into the solution in dilute caustic potash the base separates out in colorless plates melting at 75°.

	Calculated for $C_{14}H_{17}N_2SO_2$.	Found. I.	II.
C	66.5	66.3	66.35
H	6.1	5.8	5.9
N	10.1	10.3	10.3

The base is most easily identified in the form of its monoacetyl derivative, which is formed when it is boiled for a short time with acetyl chloride or acetic anhydride. It is readily soluble in alcohol and ether, difficultly soluble in water, and melts at 152°.

	Calculated for $C_{16}H_{18}N_2SO_3$.	Found. I.	II.
N	8.8	8.8	8.9

Since the acetyl derivative is still soluble in alkalies it must be acetylphenylamidoethanesulphone anilide

$$\begin{matrix}CH_2CO\\C_6H_5\end{matrix}\!\!>\!NCH_2.CH_2SO_2NHC_6H_5.$$

The mixture of salts insoluble in ether can be separated by recrystallization from absolute alcohol. One is aniline hydrochlorate melting at 192°. The other is the aniline salt of ethanedisulphonic acid, readily soluble in water and alcohol, insoluble in ether. From alcohol it crystallizes in colorless plates which do not melt without decomposition.

	Calculated for $C_{14}H_{20}N_2S_2O_6$.	Found. I.	II.
N	7.4	7.6	7.45

These same products are obtained when aniline acts upon the chloride under any other conditions, although the relative quantities vary. If aniline is allowed to drop into the molten chloride the main reaction is

$$\begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + 3C_6H_5NH_2 = \begin{matrix}CH_2\\|\\CH_2SO_2\end{matrix}\!\!>\!N.C_6H_5 + 2C_6H_5NH_2HCl + SO_2.$$

In the presence of solvents the main reaction is

$$\begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + 4C_6H_5NH_2 = \begin{matrix}CH_2NH.C_6H_5\\|\\CH_2SO_2NHC_6H_5\end{matrix} + 2C_6H_5NH_2HCl + SO_2.$$

In the presence of water a considerable quantity of the aniline salt of ethanedisulphonic acid is formed.

Reaction with Acid Amides.—It has been shown, by a number of different investigations, that acid chlorides generally react with acid amides in one of three ways, *viz.:*

(1) $RCOCl + R'CONH_2 = RCOOH + R'CN + HCl.$

(2) $RCOCl + R'CONH_2 = RCONH_2 + R'COCl.$

(3) $RCOCl + R'CONH_2 = \begin{matrix}RCO\\R'CO\end{matrix}\!\!>\!NH + HCl.$

Since the amide of ethanedisulphonic acid could not be prepared by the usual reactions, an effort was made to prepare it

indirectly by realizing the second reaction. A number of different amides were tried, but since the results were essentially the same in all cases only the experiments with acetamide will be described.

One molecule of the chloride and four molecules of acetamide were brought together in glacial acetic acid. Reaction began at once, accompanied by a slow evolution of sulphur dioxide. To complete the reaction, however, it was necessary to warm on the water-bath. After the sulphur dioxide ceased to come off, the acetic acid was removed by distillation, under diminished pressure, and subjected to fractional distillation. A fraction boiling below 90° was neutralized with sodium carbonate, extracted with ether, and again fractioned. This gave a liquid with a constant boiling-point of 81°, found to be pure acetonitrile by saponification to acetic acid. If the distillate was allowed to stand without fractioning the long spear-shaped crystals, characteristic of the hydrochloride of acetamide, $(CH_3CONH_2)_2.HCl$, separated out.

The residue left after removal of the acetic acid was boiled with absolute alcohol. A residue was pure ammonium ethanedisulphonate:

	Calculated for $C_2H_4(SO_3NH_4)_2$.	Found. I.	II.
N	12.8	12.8	12.75

The alcoholic extract contained a considerable quantity of the same salt mixed with another ammonium salt. After repeated recrystallizations from alcohol this was obtained in the form of large monoclinic plates, readily soluble in alcohol and melting at 192°.

Analysis showed that the substance is ammonium ethanesulphonate.

	Calculated for $C_2H_8ClNSO_3$.	Found. I.	II.
C	14.9	14.6	14.75
H	5.1	5.4	5.35
Cl	22.0	22.15	22.1
N	8.7	8.7	8.75
S	19.8	19.75	19.7

It is difficult to account for the formation of such a substance, from a symmetrical chloride. It was, however, re-

peatedly obtained from the pure chloride, and there can be no doubt as to its structure, since it gives sodium ethanedisulphonate when boiled with sodium sulphite.

7. Reaction of the Chloride with Salts of Organic Acids.— When the chloride is brought in contact with a salt of some organic acid in the presence of a neutral solvent, a peculiar reaction takes place, which illustrates the ease with which this substance passes into an unsaturated acid. If, for instance, a cold solution of one molecule of the chloride in glacial acetic acid is poured into a solution of four molecules of sodium acetate in the same solvent, a rapid evolution of sulphur dioxide commences in the cold, and all the chlorine is precipitated out as sodium chloride. If the acetic acid is distilled off, and the residue purified by recrystallization from alcohol it is found to consist of sodium ethanedisulphonate and the sodium salt of ethylenesulphonic acid. The latter crystallizes from alcohol in long, thin plates, readily soluble in water, difficultly soluble in 95 per cent. alcohol, insoluble in absolute alcohol. It instantly reduces permanganate and decolorizes bromine water in the cold. Analysis gave the following results:

	Calculated for $C_2H_3SO_3Na$.	Found. I.	II.
C	18.6	18.45	18.4
H	2.3	2.5	2.55
Na	17.7	17.7	17.82

The distillate, on fractioning, gave a portion which boiled considerably above the boiling-point of acetic acid, and hence must have contained acetic anhydride. The reaction probably takes place in several stages:

$$1.\quad \begin{matrix} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{matrix} + 2NaC_2H_3O_2 = \begin{matrix} CH_2SO_2OCH_3CO \\ | \\ CH_2SO_2OCH_3CO \end{matrix} + 2NaCl.$$

$$2.\ \begin{cases} \begin{matrix} CH_2SO_2O.COCH_3 \\ | \\ CH_2SO_2O.COCH_3 \end{matrix} + NaC_2H_3O_2 = \\ \qquad\qquad \begin{matrix} CH_2 \\ \| \\ CHSO_2Na \end{matrix} + (C_2H_3O)_2O + CH_3COOH + SO_2; \end{cases}$$

$$\begin{matrix} CH_2SO_2O.COCH_3 \\ | \\ CH_2SO_2O.COCH_3 \end{matrix} + 2NaC_2H_3O_2 = \begin{matrix} CH_2SO_2Na \\ | \\ CH_2SO_2Na \end{matrix} + 2(CH_3CO)_2O.$$

About 95 per cent. of the chloride used passes into a salt of the unsaturated acid, if acetic acid is used as the solvent. The reaction also takes place when alcohol is used as the solvent, but the amount of unsaturated acid obtained is considerably less. Any organic salt soluble in alcohol may be substituted for the acetate. If a difficultly soluble salt like ammonium oxalate is mixed with the chloride and a small quantity of alcohol added, the salt and the chloride go into solution and oxalic acid and ammonium chloride crystallize out.

8. *The Action of Zinc Dust.*—The action of zinc dust was studied by Otto and Casanova,[1] who obtained the zinc salt of (1,2)-ethanedisulphinic acid. As they do not state what yield of sulphinic acid was obtained, or whether any other substances are formed, their experiments were repeated. The chloride was treated with zinc dust according to the directions of Otto and Schiller,[2] the mixture being kept cool with running water. After the zinc chloride had been removed with cold water, the residue was digested with sodium carbonate, filtered and evaporated to small volume. It was then treated with aqueous alcohol which precipitated a considerable quantity of a sodium salt free from organic matter. This was found to consist mainly of sodium sulphite and sodium sulphate mixed with a small quantity of sodium carbonate. From the alcoholic solution the sodium sulphinate was obtained with the properties described by Otto. The maximum yield corresponded to 53 per cent. of the chloride. The small yield

[1] J. prakt. Chem., [2] **26**, 439. [2] Ber. d. chem. Ges., **9**, 1585.

and the formation of sodium sulphite and sodium sulphate show that a considerable quantity of the chloride reacts in a different way. The greater part of the product of this second reaction is found with the zinc chloride in the aqueous solution. As the study of this substance is still being carried on, its description will be reserved for a subsequent paper.

Summary.

I. (1, 2)-Ethanedisulphonic acid forms but one chloride which is probably symmetrical (1, 2)-ethanedisulphone chloride, $\begin{matrix} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{matrix}$.

II. (1, 2)-Ethanedisulphone chloride is stable to 160°. Above this temperature it is decomposed according to the equation: $C_2H_4(SO_2Cl)_2 = CH_2Cl.CH_2SO_2Cl + SO_2$.

III. Whenever any substance acts upon the chloride two reactions take place. The main reaction results in the formation of the lowest member of the unsaturated sulphonic acid series, $CH_2{=}CHSO_2H$, some derivative of this acid, or a derivative of ethanemonosulphonic acid. A subordinate reaction results in the regeneration of (1, 2)-ethanedisulphonic acid.

IV. When water, alcohol, and other hydroxyl compounds act upon the chloride the main product is ethylenesulphonic acid or one of its derivatives.

V. When ammonia or substituted ammonias react with the chloride a substitution-product of ethanesulphonic acid forms the main product.

VI. When acid amides react with the chloride the main product is a derivative of (1,2)-chlorethanesulphonic acid.

VII. The best way to prepare unsaturated sulphonic acids is to decompose with water the chlorides of polysulphonic acids, which have sulphonic acid residues in the 1, 2 positions with reference to each other.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE.

THE DISSOCIATION OF ELECTROLYTES AS MEASURED BY THE BOILING-POINT METHOD.

By Harry C. Jones and Stephen H. King.

The two methods of general application for measuring the amount of electrolytic dissociation in aqueous solutions, are, the conductivity method of Kohlrausch,[1] and the freezing-point method of Beckmann in its most improved forms.[2] There are, in addition, several methods available for determining the concentration of particular kinds of ions, or which admit of application to a limited number of cases, as the well-known solubility method of Nernst and Noyes.[3] The two methods which can be used satisfactorily with water solutions are, in turn, of limited applicability when other solvents are employed. The use of conductivity as a direct measure of dissociation is most satisfactory when water is used as a solvent. A difficulty which is encountered with other solvents is, that the dissociation in them is not complete at dilutions which come within the range of that method. The value of $M\infty$ cannot, therefore, be determined directly, and some assumption, which may require proof, is sometimes made in an attempt to determine its approximate value. Considerable work has, however, already been done on the conductivity of solutions of electrolytes of different concentrations in solvents other than water; notably the work of Fitzpatrick,[2] Paschkow,[2] and Völlmer,[3] on solutions in ethyl and methyl alcohol; of Zelinsky and Krapiwin[4] on solutions in methyl alcohol; and of Zanninovich-Tessarin[5] on solutions in formic acid.

The freezing-point method can also be successfully applied to only a limited number of solvents, and especially well only to water solutions. It may, perhaps, be applicable to solutions in benzene, acetic acid, and other solvents whose freezing points are not widely removed from the ordinary temperature. But many solvents do not come within its range because their points of solidification lie too low to enable one to

[1] Ann. der Phys., Wied., **26**, 161. [2] *Ibid*, **51**, 500, Ztschr. phys. Chem., **11**, 529.
[3] Ztschr. phys. Chem., **4**, 372; **6**, 241. [4] Phil. Mag., 377 (1887).
[5] Uber die Leitfähigkeit einiger Salze in alkohol Lösungen. Charkow, 1892.
[6] Ann. der Phys. Wied., **52**, 328. [7] Ztschr. phys. Chem., **21**, 35.
[8] *Ibid*, **19**, 251.

apply the freezing-point method with even a fair degree of accuracy. For such solvents it seems that the boiling-point method is the only one available, and this only when it has been worked out with sufficient accuracy to enable one to place a fair amount of confidence in the results. On the other hand, the boiling-point method is not easily applied to water solutions, owing in part to the very small value of the constant for that solvent.

One of the causes why the physical chemistry of to-day is primarily the physical chemistry of water solutions, is doubtless the greater dissociating action of that solvent. But another, which is strongly operative, is the absence of a reliable method with which to measure accurately the amount of dissociation in other solvents. This alone would show the importance attached to such determinations.

The interest in such measurements is, however, still further increased by the relation between the dielectric constants of solvents and their dissociating power, which has been pointed out on theoretical grounds for the first time in a readily accessible scientific journal, by J. J. Thomson,[1] and about the same time by W. Nernst.[2] Whether such a relation exists rigidly and quantitatively,—whether dissociating power is a function of any one physical property of the solvent, can be determined only by a careful study of the dissociation of electrolytes in the different solvents in question. In order that such work may be done, it is necessary that a method be worked out which will meet the requirements of practicability and accuracy.

The object of this preliminary notice is to call attention to the fact that we have such, in an improved form of the Beckmann boiling-point method, which he devised for the determination of the molecular weights of non-electrolytes. The essential feature in the new boiling-point apparatus[3] is the introduction of a platinum cylinder around the thermometer, which cuts off the effect of radiation, and at the same time prevents the condensed solvent from coming in contact with the thermometer until it has been reheated. The determina-

[1] Phil. Mag., **36**, 320.
[2] Göttinger Nachrichten, 1893 : and Ztschr. phys. Chem., **13**, 531.
[3] This JOURNAL, **19**, 581.

tions of the molecular weights of a number of non-electrolytes in five solvents, whose boiling-points vary from 35° to 182°, show that we have to deal with the simplest efficient boiling-point apparatus thus far constructed. We have already applied it to the measurement of the electrolytic dissociation of solutions of two electrolytes, potassium iodide and sodium acetate, in ethyl alcohol, and the results will show the degree of accuracy of which the method is capable.

The reason why the boiling-point method has not already found extensive application in measuring dissociation is, doubtless, to be sought in the fact that it has not been worked out with accuracy sufficient to enable it to be applied with a fair degree of probability.

The alcohol used in this work was dehydrated in the usual manner. It was allowed to stand for some days over quicklime, distilled and preserved in contact with anhydrous copper sulphate. The sodium acetate used was prepared by dissolving metallic sodium in water, neutralizing the sodium hydroxide formed with acetic acid, evaporating the solution of sodium acetate to dryness, and finally drying in an air-bath, above 100°, to constant weight. The results given below are distinctly tentative and solutions of both of the compounds in question will be worked over in the future with still greater care than has been possible thus far. The prime object in publishing these values at present is to show the fair agreement between the dissociation values as determined for the same substances, under the same conditions.

The Results.

SOLVENT, ALCOHOL. Molecular rise in 100 grams 11.5°.

Potassium Iodide, molecular weight 166.

Grams solvent.	Grams potassium iodide.	Grams iodide to 100 grams solvent.	Rise in boiling-point.	Molecular rise.	Dissociation. Per cent.
53.553	1.6470	3.076	0.271°	14.625	27.2
56.234	1.2945	2.302	0.200	14.419	25.4
54.533	1.080	1.9804	0.172	14.417	25.4
58.572	1.389	2.371	0.208	14.566	26.7
58.900	1.060	1.800	0.158	14.576	26.7

Sodium Acetate, molecular weight 82.1.

Grams solvent.	Grams sodium acetate.	Grams acetate in 100 grams solvent.	Rise in boiling-point.	Molecular rise.	Dissociation. Per cent.
57.599	0.747	1.2969	0.185°	11.711	1.8
57.599	1.217	2.1129	0.299	11.616	1.0
57.878	0.5997	1.0361	0.147	11.648	1.3
57.878	0.9715	1.6785	0.238	11.640	1.2

In these determinations the barometer was read every few minutes and the boiling points were corrected for any change in atmospheric pressure, however slight. While very small changes in the barometer can be neglected when the question under investigation is one of molecular weights, they must always be carefully taken into account when far more accurate measurements are necessary, as in the case of the measurement of dissociation.

It will be seen from the results that the dissociation of potassium iodide in alcohol is between one-third and one-fourth of that in water at the same dilution. This is just about the same ratio as exists between the dielectric constants of these two solvents.

The dissociation found for sodium acetate in alcohol is almost certainly too low. Indeed the metallic sodium used in preparing the hydroxide was found to contain more than a trace of potassium, and this may account in part for the very low values.

We propose to extend the application of this method to a large number of electrolytes, and to as many solvents as may be practicable.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
June, 1897.

Contributions from the Sheffield Laboratory of Yale University.

LIV.—ON DIACYL ANILIDES.

By H. L. Wheeler, T. E. Smith, and C. H. Warren.

It has frequently been observed that formanilide shows a departure from the other anilides in many of its properties, and it has been stated that this would seem to indicate that it is not an anilide or, in other words, that it does not contain the formyl group $-C\langle{H \atop O}$.

In the diacyl anilides the formyl group exists as represented above, and it seemed of interest to compare crystallographically the formyl derivative in one of these series with those of its homologues. We have, therefore, prepared the following series of diacyl anilides, and find that some of these compounds are especially suitable for a crystallographic examination:

Formylbenzenesulphanilide, $C_6H_5N\langle{CHO \atop SO_2C_6H_5}$.

Acetylbenzenesulphanilide, $C_6H_5N\langle{COCH_3 \atop SO_2C_6H_5}$.

Propionylbenzenesulphanilide, $C_6H_5N\langle{COCH_2CH_3 \atop SO_2C_6H_5}$.

n-Butyrylbenzenesulphanilide, $C_6H_5N\langle{COCH_2CH_2CH_3 \atop SO_2C_6H_5}$.

Benzoylbenzenesulphanilide, $C_6H_5N\langle{COC_6H_5 \atop SO_2C_6H_5}$.

Benzoylbenzenesulph-α-naphthalide, *Benzoylbenzenesulph-β-naphthalide*, $C_{10}H_7N\langle{COC_6H_5 \atop SO_2C_6H_5}$.

The results of the crystallographic examination of these compounds show that acetyl and propionylbenzenesulphanilide exhibit close crystallographic analogy, the compounds being monoclinic, hemimorphic, and pyroelectric, their crystallographic axes and the angle β being similar.

On the other hand, formylbenzenesulphanilide, which is orthorhombic, shows no analogy whatever with these compounds. It may be added that crystals of formanilide which we obtained show no analogy with those of acetanilide.

Since a compound with the true formyl group may exhibit

a departure in physical properties from those of the homologues it follows that a similar departure in physical properties in the case of formanilide, formic acid,[1] etc., cannot be taken as evidence against the presence of the group $-C\diagup\!\!\diagdown^{H}_{O}$ in these compounds.

Knight[2] has recently investigated the action of benzoyl chloride on benzenesulphanilide on the one hand, and of benzenesulphochloride on benzanilide on the other, with the expectation of obtaining benzoylbenzenesulphanilide if benzanilide has the normal structure. As a matter of fact, the reactions did not proceed as expected, but in both cases dibenzanilide was formed.

Believing this result to be due to the secondary action of hydrogen chloride, which is formed in both reactions, we have heated benzoylbenzenesulphanilide with dry hydrogen chloride, and have found that benzoyl chloride was liberated, and also that the diacylanilide, in the presence of benzoyl chloride, is readily converted into dibenzanilide.

The explanation of the formation of dibenzanilide in the case of Knight's experiment is therefore as follows: Benzoylbenzenesulphanilide is first formed in both cases, and a portion of this in the presence of the resulting hydrogen chloride forms benzoyl chloride, which converts the remaining benzoylbenzenesulphanilide into dibenzanilide. This is the more probable, since Knight states that in both cases the same phenomena were observed. Moreover, it has been customary to prepare diacylsulphamides by heating the sulphamides with acyl chlorides. These results are, therefore, in favor of the normal structure for benzanilide.

The diacylanilides containing the benzenesulpho groups behave with alkali precisely like the other mixed diacylanilides. In each case, so far as examined, the lower acyl group is first removed.[3]

The authors take pleasure in acknowledging their great indebtedness to Professor S. L. Penfield, under whose direction the following crystallographic results were obtained:

[1] Freer and Sherman: This JOURNAL, 18, 526. [2] This JOURNAL, 19, 152.
[3] Compare also Remsen and Palmer: This JOURNAL, 8, 243.

Experimental Part.

Formylbenzenesulphanilide, $C_6H_5N\langle{CHO \atop SO_2C_6H_5}$. —This compound was prepared by acting on phenylformimidoethyl ester with benzenesulphochloride, as previously described.[1] The structure assigned to this substance follows from its method of preparation and its subsequent decomposition with alkali. The crystals for measurement were obtained from absolute alcohol in each case. Formylbenzenesulphanilide is orthorhombic, and the following forms were observed:

a, 100	*m*, 110	*e*, 201
b, 010	*d*, 101	*p*, 111

The measurements are as follows, those marked with an asterisk being taken as fundamentals.

		Measured.		Calculated.	
a ∧ *e*, 100 ∧ 201	=	55°	53′*		
a ∧ *d*, 100 ∧ 101	=	71	15	71	17′
m ∧ *m*, 110 ∧ $1\bar{1}0$	=	67	44*		
d ∧ *d*, 101 ∧ $\bar{1}01$	=	37	25	37	25
p ∧ *d*, 111 ∧ 101	=	23	17	23	18
p ∧ *a*, 111 ∧ 100	=	72	51	72	50
p ∧ *p*, 111 ∧ $\bar{1}11$	=	34	14	34	18
b ∧ p, 010 ∧ 111	=	66	39	66	42

axes $a : b : c = 0.6711 : 1 : 1.0993$.

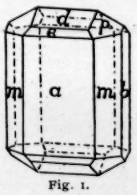


Fig. 1.

The crystals of formylbenzenesulphanilide present the habit shown in Fig. 1. They were small when compared with some of the other diacyl anilides, rarely exceeding 5 mm. in length. They have a tendency to grow in the direction of

[1] Wheeler and Walden: This JOURNAL, **19**, 135.

the c axis. On the majority of the crystals it was found that the full number of the e and d faces were not developed, thus giving the crystals a decidedly monoclinic aspect.

Acetylbenzenesulphanilide, $C_6H_5N\langle^{COCH_3}_{SO_2C_6H_5}$.—This and the following diacyl anilides were prepared by acting on the sodium salts of the sulphanilide in dry benzene with acid anhydrides. Their formation results more smoothly in this manner than when the sulphanilides are heated with acid chlorides. The structure assigned to these substances follows from their method of preparation, since Blacher[1] has shown that the sodium salt of benzamide gives with benzoic and acetic anhydrides dibenzamide and acetbenzamide, and these diacylamides have both acyl groups attached to nitrogen, as proved conclusively by Wheeler and Walden.[2]

Acetylbenzenesulphanilide separates from very dilute solutions in the form of large, rough, colorless, monoclinic plates, having a tendency to form clusters. From more concentrated solutions small, finely developed crystals, 1 to 2 mm. in length grow, while from still more concentrated solutions the substance comes down in long thin needles. When the material was crystallized from alcohol it melted constantly at 116°.5. A nitrogen determination gave the following result :

	Calculated for $C_{14}H_{13}NO_3S$.	Found.
N	5.09	4.91

The crystals are hemimorphic, as shown in Fig. 2. The forms observed are :

a, 100	s, $\bar{1}01$	p, $\bar{1}11$
b, 010	d, 011	
c, 001	d_1, $0\bar{1}1$	

The faces b, d, and p were observed at that extremity of the b axis, where negative electricity developed, when the crystals, which had been heated for some time, were cooled, while at the other extremity d alone occurred.

The measurements obtained are as follows :

[1] Ber. d. chem. Ges., **28**, 2356. [2] *Loc. cit.*

		Measured.		Calculated.	
$a \wedge c$, 100 $\wedge$ 001	=	64°	56′*		
$d \wedge d$, 011 $\wedge$ 01$\bar{1}$	=	75	59*		
$c \wedge s$, 001 $\wedge$ $\bar{1}$01	=	63	56*		
$c \wedge d$, 001 $\wedge$ 011	=	51	59	52°	01½′
$a \wedge d$, 100 $\wedge$ 011	=	75	0	74	52
$a \wedge p$, $\bar{1}$00 $\wedge$ $\bar{1}$11	=	64	52	65	2
$p \wedge d$, $\bar{1}$11 $\wedge$ 011	=	40	8	40	6
$s \wedge p$, $\bar{1}$01 $\wedge$ $\bar{1}$11	=	47	44		
$p \wedge d$, 11$\bar{1}$ $\wedge$ 011	=	84	48	84	49

Axes = $a : b : c$ = 1.225 : 1 : 1.4138. β = 100 $\wedge$ 001 $\wedge$ 64°–59°.

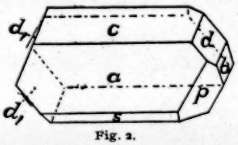


Fig. 2.

Propionylbenzenesulphanilide, $C_6N_5N\langle^{COCH_2CH_3}_{SO_2C_6H_5}$.—The product of the action of propionic anhydrid on sodium benzenesulphanilide was crystallized from absolute alcohol when it melted constantly at 115°.

	Calculated for $C_{15}H_{15}NO_3S$.	Found.
N	4.8	4.7

The crystals are hemimorphic, Fig. 3, representing the prevailing habit, while more complicated crystals, like Fig. 4, were only occasionally found.

The forms observed are:

a, 100	c, 001	d_1, 0$\bar{1}$2
b, 010	n, 3$\bar{1}$0	x, 31$\bar{2}$
b_1, 0$\bar{1}$0	d, 012	x_1, 3$\bar{1}\bar{2}$

The faces x_1 and n_1 are developed at that extremity of the b axis, where positive electricity occurs, when the crystals which had been heated for some time were cooled. The face

x, when observed, was always smaller than x_1, while b and d were about equal in size to b_1 and d_1.

The measurements are as follows:

		Measured.		Calculated.	
$a \wedge d$, 100 $\wedge$ 012	=	69°	7′*		
$d \wedge d$, 012 $\wedge$ 01$\bar{2}$	=	64	46*		
$a \wedge x$, 100 $\wedge$ 31$\bar{2}$	=	38	59*		
$a \wedge c$, 100 $\wedge$ 001	=	65	0	65°	2′
$b \wedge x$, 010 $\wedge$ 31$\bar{2}$	=	68	52	68	52
$a \wedge n_1$, 100 $\wedge$ 3$\bar{1}$0	=	19	33	19	31
$c \wedge x$, 00$\bar{1}$ $\wedge$ 31$\bar{2}$	=	82	0	82	0
$c \wedge n_1$, 001 $\wedge$ 3$\bar{1}$0	=	66	32	66	33
$b \wedge n_1$, 010 $\wedge$ 3$\bar{1}$0	=	70	27	70	29
$d \wedge x_1$, 0$\bar{1}$2 $\wedge$ 3$\bar{1}$2	=	71	54	71	55

Axes = $a : b : c$ = 1.170 : 1 : 1.390. β = 100 $\wedge$ 001 = 65° 2′.

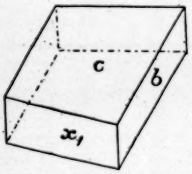


Fig. 3.

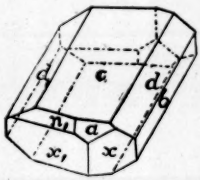


Fig. 4.

From very dilute solutions, containing only a few grams of material, this compound grows in crystals enormously elongated in the direction of the a axis, some of the crystals attaining a length of 75 mm. and a diameter of from 2 to 3 mm. On account of the fact that these crystals show entirely different habits from those of the acetyl compounds, it was thought at first that no analogy in crystalline structure existed between them. By adopting, however, appropriate indices for the faces, a close similarity in the axial ratios of these hemimorphic compounds may be observed as follows:

Acetyl $a : b : c = 1.225 : 1 : 1.4138$. $\beta = 64° 56'$.
Propionyl $a : b : c = 1.170 : 1 : 1.390$. $\beta = 65° 2'$.

n-Butyrylbenzenesulphanilide, $C_6H_5N\langle^{COCH_2CH_2CH_3}_{SO_2C_6H_5}$.—This compound, prepared in the same manner as the acetyl and propionyl compounds, gave stout prisms when crystallized from alcohol, melting at 89°–90°. Satisfactory measurements, for a crystallographic description, were not obtained. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}NO_3S$.	Found.
N	4.62	4.38

Benzoylbenzenesulphanilide, $C_6H_5N\langle^{COC_6H_5}_{SO_2C_6H_5}$.—The crystals of this compound were small and well developed when grown from a dilute solution, not being more than 2 mm. in length. From more concentrated solutions it comes down in long, thin needles. It was found that the crystals of this compound were monoclinic but showed no hemimorphic or pyroelectric properties. When crystallized repeatedly from alcohol they melt from 114°–115°, and a nitrogen determination gave the following results :

	Calculated for $C_{19}H_{15}NO_3S$.	Found.
N	4.15	4.29

The forms observed are :

b, 010 *c*, 001 *m*, 110 *l*, 120 *x*, $\bar{1}01$

The measurements obtained are the following :

		Measured.		Calculated.	
$c \wedge x$, 001 $\wedge \bar{1}01$	=	80°	18′*		
$c \wedge m$, 001 $\wedge$ 110	=	61	50 *		
$m \wedge m$, $1\bar{1}0 \wedge$ 110	=	68	56 *		
$m \wedge l$, 110 $\wedge$ 120	=	19	26	19°	27′
$c \wedge l$, 001 $\wedge$ 120	=	70	19	70	17
$m \wedge x$, 110 $\wedge 10\bar{1}$	=	54	3	54	5
$l \wedge x$, 120 $\wedge 10\bar{1}$	=	64	34	65	0

Axes $a : b : c = 0.8373 : 1 : 1.175$. $\beta = 100 \wedge 001 = 55° 4'$.

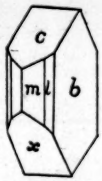


Fig. 5.

Figure 5 represents the prevailing habit of benzoylbenzenesulphanilide. No close crystallographic relation was found between this compound and the preceding ones.

A small quantity of the above compound was heated in a test-tube to 180°. Dry hydrogen chloride was passed in and benzoyl chloride was formed. When the diacylanilide was heated with benzoyl chloride to 180° for ten hours a reddish oil was obtained, which solidified on cooling. This was crystallized from alcohol when a mass of colorless needles was obtained, melting from 160°–161°. A nitrogen determination gave 4.93 per cent. of nitrogen, while the calculated percentages for benzanilide and dibenzanilide are 7.07 and 4.65, respectively. The material formed by this treatment was therefore dibenzanilide.

Benzenesulph-α-naphthalide, $C_{10}H_7NHSO_2C_6H_5$.—This was obtained by the Baumann-Schotten reaction in the usual manner. When crystallized from alcohol it separated in needles and melted from 168°–169°. A nitrogen determination gave :

	Calculated for $C_{16}H_{13}NO_2S$.	Found.
N	4.94	4.47

Benzoylbenzenesulph-α-naphthalide, $C_{10}H_7N\langle\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}$.—The crude material in this case was purified by boiling with absolute alcohol, washing with sodium hydrate, and then crystallizing from a mixture of benzene and ligroïn. It formed minute crystals, which melted constantly at 193°–194°, and which seemed to be pure. Nitrogen determinations in different samples, however, invariably came low.

	Calculated for $C_{22}H_{17}NO_3S$.	Found. I.	II.	III.	IV.
N	3.61	2.78	3.05	2.72	2.90

Benzenesulph-β-naphthalide, $C_{10}H_7NHSO_2C_6H_5$.—This material crystallized poorly from dilute alcohol in small, oblong plates or flattened prisms, which apparently melted constantly at 97°.

	Calculated for $C_{16}H_{13}NO_2S$.	Found.
N	4.9	4.7

Benzoylbenzenesulph-β-naphthalide, $C_{10}H_7N\langle^{COC_6H_5}_{SO_2C_6H_5}$.—This consisted of minute, fine, white needles, melting from 161°–162°.

	Calculated for $C_{23}H_{17}NO_3S$.	Found.
N	3.6	3.4

Formanilide, C_6H_5NHCHO.—The crystals for examination in this case were prepared by spontaneous evaporation of a solution of the anilide in a mixture of low-boiling ligroïn and ether. This gave monoclinic crystals about 6 or 7 mm. in length, and the following forms were observed:

a, 100 *c*, 001 *e*, 101 *d*, 011 *p*, 112

The measurements obtained were as follows:

		Measured.		Calculated.	
$c \wedge e$, 001 ∧ 101	=	26°	17′*		
$a \wedge c$, 100 ∧ 001	=	85	6*		
$c \wedge d$, 001 ∧ 011	=	67	20		
$a \wedge e$, 100 ∧ 101	=	58	52	58°	49′
$d \wedge d$, 011 ∧ $01\bar{1}$	=	45	24	45	20
$a \wedge d$, 100 ∧ 011	=	87	57	88	6
$e \wedge d$, 101 ∧ 011	=	80	8½	80	10½
$p \wedge p$, 112 ∧ $\bar{1}12$	=	83	8	83	0

Axes = $a : b : c = 2.188 : 1 : 2.403$. $\beta = 100\frac{3}{4} \wedge 001 = 85°\ 6'$.

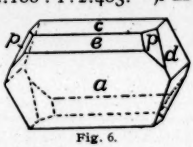


Fig. 6.

The crystals of formanilide were for the most part imperfect and gave poor reflections. Acetanilide has been measured by Bücking,[1] and was found to be orthorhombic, the axes $a : c = 0.848 : 2.067$.

NEW HAVEN, May, 1897.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XVII.–SYNTHESIS OF HEXAMETHYLENE-GLYCOL DIETHYL ETHER AND OTHER ETHERS FROM TRIMETHYLENE GLYCOL.

BY ARTHUR A. NOYES.

INTRODUCTION.

The following investigation was undertaken originally with the hope of preparing the hydrocarbon hexamethylene[2] from compounds of the fatty series. Although this object has not been attained, yet the syntheses which have been effected seem of sufficient interest to merit publication.

Trimethyleneglycol formed the starting point in this investigation. This substance was discovered last year by Noyes and Watkins[3] to exist as an accidental impurity in a sample of low-gravity glycerin recovered from soap-lye, and a considerable quantity of it was obtained from that source. It was submitted to the series of reactions that are represented by the following equations, hexamethyleneglycol diethyl ether, $C_2H_4O.(CH_2)_6.OC_2H_5$, being finally obtained:

$$CH_2OH.CH_2.CH_2OH + Na = CH_2OH.CH_2.CH_2ONa + H;$$
$$CH_2ONa.CH_2.CH_2OH + C_2H_5I = C_2H_4O.(CH_2)_3.OH + NaI;$$
$$3C_2H_4O.(CH_2)_3.OH + PCl_3[Br_2][I_2] =$$
$$3C_2H_4O.(CH_2)_3.Cl[Br][I] + PO_2H_3.$$
$$2C_2H_4O.(CH_2)_3.Cl[Br][I] + 2Na = C_2H_4O(CH_2)_6.OC_2H_5 + 2NaCl[Br][I].$$

Hexamethyleneglycol diethyl ether was also probably obtained, though not in a state of purity, from the ethyl brompropyl ether by the following series of reactions:

[1] Jahresb. 1877, 679. [2] Cf. Baeyer: Ann. Chem., **278**, 110.
[3] J. Am. Chem. Soc., **17**, 890.

$C_2H_5O.(CH_2)_3.Br + KCN = C_2H_5O.(CH_2)_3.CN + KBr.$

$C_2H_5O.(CH_2)_3.CN + KOH + H_2O = C_2H_5O.(CH_2)_3.CO_2K + NH_3$

$2C_2H_5O.(CH_2)_3.CO_2K + 2H_2O$ (electrolyzed) =

$C_2H_5O.(CH_2)_6.OC_2H_5 + 2KHCO_3 + H_2.$

In addition to the compounds involved in these syntheses, a number of others have been prepared from the ethyl γ-brom-propyl ether. As the reactions of halogenated ethers have been but little investigated, the results may be of interest. The malonic-ether and Fittig syntheses have both been successfully carried out with the brom-ether referred to.

The separate preparations will be described in detail in the following pages:

Trimethyleneglycol Monoethyl Ether,

$CH_2OH.CH_2.CH_2.OC_2H_5.$

In the first attempts to prepare this substance, the theoretical quantity (one atomic weight of sodium), was dissolved in one molecular weight of glycol with the aid of heat, and the product was then heated on a water-bath with an excess of ethyl iodide. The sodium glycolate formed was completely solid, and the ethyl iodide acted very slowly upon it. The result was entirely unsatisfactory.

It was, however, found that by employing about half the theoretical quantity of sodium a fairly good yield was obtained. To 300 grams of glycol in a 500 cc. distilling-flask 42 grams of very thin-cut sodium are added continuously in small portions so that the temperature of the mixture is maintained at, but not much above, the melting-point of the sodium. If the addition is made too rapidly, violent heating attended by decomposition, results. If too slowly, the action ceases, and external heat must be applied to start it again, an operation often attended with serious frothing. Only towards the very end of the reaction is it sometimes necessary to heat gently over a free flame to dissolve the last of the sodium. The product, when cold, is a yellow transparent, barely fluid mass. The flask containing it, provided with a long return-cooler, is heated in a water-bath, and 318 grams of ethyl iodide are added, cautiously at first. The mixture is heated for two or three hours longer, and is then submitted to distillation in an

oil-bath, at first at ordinary and finally under greatly reduced pressure. For the complete distillation several hours are necessary: The distillate is then fractionated at ordinary pressure, a tower being used up to 190°. The principal fractions boiled between 70° and 90°, 150°–170°, and 210°–215°. In some cases a considerable amount of material boiling above 230° was also formed. The first fraction consisted mainly of unchanged ethyl iodide and ethyl alcohol, the second of the monoethyl ether, and the third of the glycol. From 600 grams of glycol 234 grams of the ether boiling between 150° and 170°, and 341 grams of recovered glycol were obtained. The yield referred to the glycol consumed is 66 per cent. of the theoretical. The portion boiling between 150°–170° was repeatedly refractionated, and it finally boiled almost wholly between 159° and 162°. The fraction from 160°–161° (corr.) was analyzed with the following results:

0.3811 gram of substance gave 0.8040 gram CO_2 and 0.3970 gram H_2O.

	Calculated for $C_5H_{12}O_2$.	Found.
C	57.69	57.58
H	11.59	11.66

The trimethylene-glycol monoethyl ether is a colorless, pleasant-smelling liquid, miscible with water in all proportions. Its specific gravity at $\frac{25°}{15°}$ was found to be 0.915, and its index of refraction at 25°, 1.416. Its boiling-point is 160°–161° (corr.) at 760 mm.

Trimethylene-glycol Diethyl Ether

$C_2H_5O.CH_2.CH_2.CH_2.OC_2H_5$.

(With H. M. CHASE.)

The diethyl ether was prepared from the monoethyl ether by a process exactly similar to that described above, 55 grams of monoethyl ether, 6 grams of sodium, and 45 grams of ethyl iodide being used. The distillate boiling above 100° was washed repeatedly with water to remove the monoethyl ether, dried with potassium carbonate, and distilled. The portion from 130°–150° was allowed to stand over sodium, nad was then twice distilled from it.

The product, consisting of 5 grams, finally distilled mainly between 140°–141° (corr.) at 760 mm., and was submitted to analysis with results as follows:

0.4154 gram substance gave 0.9609 gram CO_2 and 0.4554 gram H_2O.

0.3231 gram substance gave 0.7485 and 0.3496 gram H_2O.

	Calculated for $C_7H_{14}O_2$.	Found. I.	II.
C	63.58	63.14	63.23
H	12.20	12.27	12.11

The diethyl ether possesses a fruity odor, and is insoluble in water. The specific gravity at $\frac{25°}{25°}$ is 0.835.

Ethyl γ-Chlorpropyl Ether, $CH_2Cl.CH_2.CH_2.OC_2H_5$.

This compound was prepared by the action of phosphorus trichloride on trimethyleneglycol monoethyl ether. To 82 grams of the latter 49 grams of the former were gradually added, the mixture allowed to stand for some hours in cold water, and then heated on a water-bath for one hour. The product was poured into water, washed, dried with calcium chloride, and distilled. 50 grams of the chlorether boiling between 125° and 135° were obtained, or about 50 per cent. of the theoretical yield.

Subsequent fractionation showed that the true boiling-point is 130°–131 (corr). The specific gravity at $\frac{25°}{25°}$ was found to be 0.957.

The compound was analyzed with the following result:

0.3643 gram substance gave 0.6552 gram CO_2 and 0.3096 gram H_2O.

0.3887 gram substance gave 0.7060 gram CO_2 and 0.3239 gram H_2O.

	Calculated for $C_5H_{11}ClO$.	Found. I.	II.
C	48.98	49.07	49.57
H	9.04	9.53	9.32

Ethyl γ-Brompropyl Ether, $CH_2Br.CH_2.CH_2.OC_2H_5$.

The method of preparation was the same as in the case of the preceding compound. Equal quantities (105 grams of

each) of phosphorus tribromide and the monoethyl ether were used. From 210 grams of the latter worked in two separate operations 246 grams of the bromether boiling between 148° and 153° were obtained, amounting to 73 per cent. of the theoretical yield. It is advisable in order to avoid decomposition to fractionate the ether under reduced pressure with the help of a tower. A small quantity of ethyl bromide and of trimethylene bromide is always formed in the reaction.

The ethyl brompropyl ether is an aromatic-smelling liquid insoluble in water. Its boiling-point is 150°–151°, and its specific gravity at $\frac{25}{4}^{\circ}$ is 1.300. An analysis of the ether was made by Mr. L. H. Goodhue with the following results:

0.2025 and 0.2495 gram substance gave respectively 0.2300 and 0.2828 gram AgBr.

	Calculated for $C_5H_{11}BrO$.	Found. I.	II.
Br	47.83	48.30	48.20

The results are slightly high, probably owing to the presence of a small amount of trimethylene bromide, which could not be separated by fractionation.

Ethyl γ-Iodopropyl Ether, $CH_3I.CH_2.CH_2.OC_2H_5$.

(With Grace A. VanEveren.)

This ether was first prepared by a method similar to that used for the corresponding chlor- and bromethers, that is to say, by the action of phosphorus di-iodide[1] on trimethylene glycol monoethyl ether. To 60 grams of the latter compound contained in a flask surrounded with ice-water 100 grams of the di-iodide were gradually added, and the mixture was then heated on a water-bath for an hour. The resulting liquid was poured into water, washed, taken up with ether, dried with calcium chloride, and repeatedly fractionated under a pressure of 150 mm.

The product, consisting in two preparations of 30 and 40 grams respectively, distilled mainly between 130° and 134° at the pressure just mentioned, and proved to be the ethyl iodopropyl ether. This substance is a colorless liquid, turning brown on standing, possessing an odor exactly like that of the corresponding chlor- and bromethers. Its specific grav-

[1] Made as described in Graham-Otto's Lehrbuch der Chemie, 2, 340.

ity at $\frac{25°}{15°}$ was found to be 1.585. It is completely soluble in cold concentrated sulphuric acid, and separates unchanged from the solution when diluted with water. Carius determinations gave the following results:

0.2123 and 0.2215 gram substance gave respectively 0.2398 and 0.2488 gram of silver iodide.

	Calculated for $C_8H_{17}IO$.	Found. I.	Found. II.
I	59.30	61.05	60.70

The somewhat too high results are probably explained by the presence of a small amount of trimethylene iodide. The yields of the iodether (30 and 40 grams from 60 grams of the glycol monoethyl ether) were not very satisfactory, being only 25 and 33 per cent. of the theoretical yield.

In the hope of getting a better yield, an attempt was made to prepare the ethyl iodpropyl ether by another method, namely by saturating the glycol monoethyl ether at 0° with hydriodic acid, and allowing the mixture to stand, in one case for half an hour and in another for several hours, at the ordinary temperature. It was, however, found that the products (after washing with alkali and drying) had specific gravities of 1.92 and 1.98, respectively, showing that a large proportion of di-iodide had been formed, and that even in the cold the ethoxyl, as well as the hydroxyl, group had been replaced by iodine. As further evidence of this, it may be mentioned that a large amount of a low-boiling iodide (ethyl iodide) was obtained on distilling the product from a water-bath.

Hexamethylene-glycol Diethyl Ether, $C_2H_5O(CH_2)_6OC_2H_5$.

The only investigation known to me of the action of sodium or other metals on halogenated ethers is that of Henry,[1] who experimented with β-ioddiethyl ether in this direction. His experiments were undertaken in the hope of effecting the synthesis of tetramethylene-glycol diethyl ether by the union of the radicals left on the removal of the iodine from two molecules. His experiments were, however, entirely unsuccessful in this respect.

Nevertheless, I thought it worth while to attempt the analogous synthesis of hexamethylene-glycol diethyl ether from

[1] Compt. rend., **100**, 1007.

the halogenated propyl ethyl ethers. All three of these were therefore treated with sodium. The experiments, which were made in a similar manner in the three cases, were carried out as follows :

A third or half more than the theoretical quantity of sodium required for the decomposition of the halogenated ether was cut in thin slices, placed in a flask, and covered with absolute ether ; the total quantity of the halogenated ether was then added at once, and the mixture heated on a water-bath for several hours. The liquid was decanted from the precipitated sodium haloid, filtered, and distilled, a tower being used until the boiling-point reached 70°.

Result with the Chlorether.—The product of the reaction with the chlorether separated into three fractions, boiling from 65°–68°, from 125°–135°, and 207°–209° (corr.) at the ordinary pressure.

The last portion, as will be seen later, consisted of hexamethylene-glycol diethyl ether. It was, however, very small in amount, only 3½ grams having been obtained from 72 grams of chlorether worked in two operations. Its specific gravity at $\frac{25°}{25°}$ was found to be 0.847.

The fraction boiling from 125°–135° was unchanged chlorether. That from 65°–68° was, however, evidently a product of the reaction. Its odor was exactly like that of ordinary ethyl ether ; it was not miscible with water, and did not decolorize bromine water ; its specific gravity was 0.727. These facts showed that the body was probably ethyl propyl ether, whose boiling-point is 64°, and whose specific gravity is 0.735 at 20°.

The reaction was carried out several times under various conditions (of temperature and proportions of the sodium, chlorether, and ordinary ether), but no better yield of hexamethylene-glycol diethyl ether than that above mentioned could be obtained.

Result with the Bromether.—In the case of the ethyl brompropyl ether the result was somewhat more satisfactory. The reaction-product resolved itself mainly into two fractions, boiling from 130°–150° and from 200°–220°.[1] In one experi-

[1] A small quantity of liquid boiling from 40°–60° lighter than water, insoluble in it, and combining energetically with bromine, was also obtained.

ment in which 83 grams of bromether were employed, the former fraction consisted of 11 cc. and the latter of 9 cc. In a second experiment with 111 grams of bromether they consisted respectively of 18 and 6 cc. In a third operation with a larger amount (214 grams) of bromether, 32 grams of the higher boiling portion, consisting of methylene-glycol diethyl ether, were obtained. This is 28 per cent. of the theoretical yield.

That this high-boiling portion was, in reality, the expected hexamethyleneglycol diethylether is shown by the following analyses made with a portion of the substance purified by fractionation under reduced pressure, since slight decomposition takes place at ordinary pressure.

0.4479 gram substance gave 1.1270 grams CO_2, and 0.5013 gram H_2O.

0.5074 gram substance gave 1.2744 grams CO_2, and 0.5723 gram H_2O.

	Calculated for $C_{10}H_{22}O_2$.	Found. I.	II.
C	68.92	68.66	68.52
H	12.74	12.53	12.62

An attempt to make a vapor density determination by the Victor Meyer method in naphthalene vapor was unsuccessful, owing to rapid decomposition of the substance.

The hexamethylene-glycol diethyl ether, as obtained, was a colorless liquid insoluble in water. It boils at 208° (corr.) at 760 mm., and at 160°–162° (corr.) at 200 mm. Its specific gravity at $\frac{25°}{25°}$ is 0.846. It dissolves in cold concentrated sulphuric acid and is precipitated from the solution by the addition of water. It is slowly acted upon in the cold by sodium with formation of a slimy green solid, and the small yield obtained is no doubt due, at least in part, to this fact. Phosphorus trichloride heated with it on a water-bath for two hours had little or no action upon it.

The original fraction, boiling from 130°–150°, was diluted with ether and boiled with a large excess of sodium to remove all traces of unchanged bromether present in it. On refractionation the product boiled almost wholly between 140° and 143°, and this portion was further examined. Its specific

gravity was 0.797. It contained 70.8 per cent. of carbon, 12.4 per cent. of hydrogen, and 16.8 per cent. of oxygen. Its vapor density determined in naphthalene vapor was 2.85, corresponding to a molecular weight of 82. Its behavior with cold concentrated sulphuric acid showed it, however, to be a mixture. It dissolved completely in that reagent, but on dilution with water only one-fourth of the original liquid precipitated, the remainder having combined chemically with the acid. The precipitated portion was evidently an ether, probably trimethylene-glycol diethyl ether, which corresponds in odor and boiling-point with those shown by this substance. Its formation from the ethyl brompropyl ether is readily explained by the assumption that sodium ethylate was produced in the sodium reaction either from alcohol present in the absolute ether employed or by decomposition of the bromether itself.

The nature of the other and main constituent of the 140°–143° fraction could not be determined. It was evidently an unsaturated body, for the original liquid decolorized instantly aqueous bromine, and also a solution of iodine. It is remarkable that with dry bromine hydrobromic acid was copiously evolved, showing that substitution also took place.

Result with the Iod-ether.—The product was boiled with a small amount of alcoholic potash to free it entirely from unchanged iod-ether; it was then precipitated from the solution by the addition of water, and was dried and distilled. It boiled between 157° and 162° at 200 mm. pressure and had a specific gravity of 0.843 at $\frac{23°}{23°}$. It gave the following results on analysis:

0.2668 gram substance gave 0.6643 gram CO_2, and 0.2844 gram H_2O.

0.3004 gram substance gave 0.7493 gram CO_2 and 0.3424 gram H_2O.

	Calculated for $C_{16}H_{32}O_2$.	Found. I.	Found. II.
C	68.90	67.94	68.08
H	12.73	11.92	12.75

Three grams of the hexamethyleneglycol diethyl ether were obtained from 25 grams of the iodoether, which is 30 per cent. of the theoretical yield.

γ-Ethoxybutyric Acid, $C_2H_5O(CH_2)_3CO_2H$.

(With L. H. Goodhue.)

In order to effect the synthesis of hexamethylene-glycol diethyl ether by the second process outlined in the introduction, it was first necessary to prepare the γ-ethoxybutyric acid. This body had been previously made by Fittig and Ström[1] by the action of sodium ethylate on butyrolactone. We succeeded in obtaining it in moderate yield by the action of potassium cyanide on γ-brompropyl ethyl ether and subsequent saponification of the nitrile.

Fifty grams of the bromether were dissolved in a small quantity of alcohol, a concentrated aqueous solution of 22 grams of pure potassium cyanide (15 per cent. more than the theoretical quantity) was added, and the mixture, which consisted of two separate layers, heated in a boiling water-bath for four hours. The nitrile was not isolated, but was directly saponified by decanting the liquid containing it from the potassium bromide which had separated, adding an excess of solid caustic potash and a little water, and heating on a water-bath as long as ammonia was evolved. The alcohol was then distilled off and the solution acidified with strong hydrochloric acid, decanted from the precipitated potassium chloride, and extracted 15 times with ether.

The ether solution was dried with calcium chloride and distilled. After the removal of the ether the thermometer rose rapidly to 230°, and the product distilled almost entirely between 230° and 240° (corr.).

The properties of the product are identical with those described by Fittig and Ström, who give 232° as its boiling-point. It is a colorless liquid soluble in water.

In two separate preparations 10 grams and 15 grams of the acid were obtained from 50 and 75 grams, respectively, of the bromether, constituting in each case 25 per cent. of the theoretical yield. In another preparation, on a smaller scale (in which 15 grams of the bromether were employed) a 42 per cent. yield was obtained. The poor yield is mainly owing to the fact that a considerable portion of the ether is carbonized or resinified by the action of the potassium cyanide.

[1] Ann. Chem. (Liebig), **267**, 200.

Electrolysis of γ-Ethoxybutyric Acid.

(With L. H. Goodhue.)

The electrolysis of the acid was carried out according to the method described by Crum Brown, and Walker,[1] and used by them in the synthesis of the compound ethers of dibasic acids.

Fifteen grams of the γ-ethoxybutyric acid were neutralized with potassium carbonate and the resulting salt dissolved in the smallest possible quantity of water. The solution was placed in a large platinum crucible, which served as the cathode, and a thick platinum wire, in the form of a spiral, was placed in the center to act as an anode. The crucible was surrounded with ice-water, and a current of 3 amperes was passed through for an hour and a half. The oily layer which had formed was separated in a separatory funnel from the aqueous solution, which latter was used for dissolving another portion of the ethoxybutyric acid to be electrolyzed. The oily layer was dried with calcium chloride and submitted to distillation under a reduced pressure of 195 mm. It did not boil very constantly at first, but a portion of 4 grams was obtained after several fractionations, distilling between 155° and 165°. The quantity was not sufficient to admit of complete purification, and the following analyses will be seen to correspond only very roughly with the values calculated for hexamethyleneglycol diethyl ether.

0.3404 gram substance gave 0.8074 gram CO_2, and 0.3594 gram H_2O.

0.3085 gram substance gave 0.7355 gram CO_2, and 0.3299 gram H_2O.

	Calculated for $C_{10}H_{22}O_2$.	Found. I.	II.
C	68.90	64.74	65.06
H	12.73	11.82	11.97

But considering also the agreement of the boiling-point with that shown by the ether prepared by the sodium reaction above described, there is little doubt that the product consisted in the main of hexamethylene-glycol diethyl ether.

The yield was, however, small, only 4 grams of the ether being obtained from 30 grams of acid, which is 20 per cent. of the theoretical.

[1] Ann. Chem. (Liebig), **261**, 107.

Attempt to Prepare a Metallic Derivative from the Ethyl Brompropyl Ether.

(With L. H. Goodhue.)

No attempt has been made to our knowledge to prepare a metallic derivative of a hydrocarbon radical containing the ether grouping. We therefore investigated the action both of sodium amalgam and of the zinc-copper couple on ethyl brompropyl ether, carrying out the reactions in the manner usually followed in the preparation of mercury and zinc ethyl. The metals had no action on the bromether in the cold; they were therefore heated with it in a water-bath for several hours, a little ethyl acetate being added to promote the reaction. Even under these circumstances the action was slight, and no evidence of the formation of a metallic compound could be obtained either by distillation under reduced pressure, by extraction with ether, or by treatment with water. The presence of the ether grouping seems therefore to prevent the union of the hydrocarbon radical with metals.

Ethyl γ-Phenylpropyl Ether, $C_6H_5.CH_2.CH_2.CH_2.OC_2H_5$.

(With H. H. Tozier.)

The following experiments were made in order to determine whether the Fittig reaction can be carried out satisfactorily with a halogenated ether.

45 grams of sodium and 150 cc. of absolute ether were placed in a flask surrounded with ice-water, and a mixture of 95 grams of ethyl brompropyl ether and 114 grams of brombenzene was added in small portions, since the action when once started becomes very violent. After standing twenty-four hours the ether was distilled off on a water-bath, and the residue was then heated in an oil-bath, the pressure within the flask being reduced to 40–50 mm. The distillate was repeatedly fractionated at ordinary pressure. The principal fraction obtained boiled constantly between 222° and 226° (corr.), and consisted of 47.5 grams. The adjacent fractions (218°–222° and 226°–230°) together contained only 2.5 grams. The yield (50 grams) is 54 per cent. of the theoretical amount obtainable from the bromether taken. That this substance consisted of the expected ethyl phenylpropyl ether is shown by the following analysis:

0.2135 gram substance gave 0.6279 gram of CO_2 and 0.1879 gram of H_2O.

0.2312 gram substance gave 0.6821 gram of CO_2 and 0.2023 gram of H_2O.

	Calculated for $C_{11}H_{14}O$.	Found. I.	II.
C	80.45	80.26	80.52
H	9.82	9.85	9.79

Ethyl γ-phenylpropyl ether is a liquid of terpene-like odor of boiling-point 224° (corr.) and specific gravity 0.924 at $\frac{15°}{15°}$.

In addition to this product, 27 grams of a liquid boiling quite uniformly between 80° and 150° were obtained, but even after a second treatment with sodium no constant-boiling substance could be separated from it.

γ-Ethoxypropyl-malonic Ether,

$$C_2H_5O.(CH_2)_3.CH.(CO_2C_2H_5)_2.$$

(With C. H. Stone.)

The introduction of the radical of the ethyl brompropyl ether into malonic ether was effected in the usual manner. 48 grams of malonic ether were added to the solution of 6.9 grams of sodium in alcohol, and 50 grams of ethyl brompropyl ether gradually poured in. The mixture was then heated on a water-bath for three hours, after which the alcohol was distilled off and the residue submitted to distillation in a metal-bath under reduced pressure. The distillate was fractionated at ordinary pressure. A portion of 25 grams boiling between 270° and 275° (corr.) was thus obtained. Analysis showed it to be pure ethoxypropyl-malonic ether.

0.2104 gram substance gave 0.4505 gram CO_2 and 0.1707 gram H_2O.

0.2321 gram substance gave 0.4975 gram CO_2 and 0.1852 gram H_2O.

	Calculated for $C_{13}H_{22}O_5$.	Found. I.	II.
C	58.52	58.44	9.10
H	9.00	58.50	8.93

The ether thus prepared is a nearly odorless liquid, insoluble in water, of specific gravity 1.016 at $\frac{15°}{15°}$, and of boiling-point 273° (corr.).

The yield (25 grams from 50 grams of the bromether) is 34 per cent. of the theoretical quantity.

δ-Ethoxyvalerianic Acid, $C_2H_5O.(CH_2)_4.CO_2H$.

(With C. H. Stone.)

The ether just described was converted into δ-ethoxyvalerianic acid by boiling it with strong potassium hydrate solution (1 : 2) till the oil dissolved, acidifying the solution with hydrochloric acid, extracting a large number of times with ether, distilling off the ether, and heating the remaining liquid in an oil-bath to 170° (for about four hours) as long as carbon dioxide escaped. The impure product was fractionated and was found to resolve itself almost wholly into two fractions nearly equal in amount, and boiling from 247° to 257° (corr.), and from 209° to 212° (corr.) respectively. The former portion consisted of δ-ethoxyvalerianic acid, as its properties and the following analyses showed :

0.1738 gram substance gave 0.3647 gram CO_2 and 0.1502 gram H_2O.

0.2229 gram substance gave 0.4705 gram CO_2 and 0.1958 gram H_2O.

	Calculated for $C_7H_{14}O_3$.	Found. I.	Found. II.
C	57.50	57.25	57.58
H	9.58	9.68	9.83

The acid is a colorless liquid, soluble in water, of specific gravity 0.994, and boiling-point 252°. A 37 per cent. yield was obtained in its preparation as above described.

The nature of the compound composing the lower-boiling fraction could not be fully determined with the amount at our disposal. It was insoluble in water and in sodium carbonate solution. It was therefore completely freed from ethoxyvalerianic acid by washing with a solution of sodium carbonate. The following analyses show that it agrees approximately in percentage composition with the formula $C_7H_{14}O_3$, which would make it an isomer of ethoxyvalerianic acid.

0.1848 gram substance gave 0.3960 gram CO_2 and 0.1563 gram H_2O.

0.3181 gram substance gave 0.6791 gram CO_2 and 0.2708 gram H_2O.

	Calculated for $C_7H_{14}O_3$.	Found. I.	II.
C	57.50	58.48	58.28
H	9.58	9.46	9.53

The liquid was unacted upon by sodium in the cold, and very slightly, if at all, by a solution of potassium hydrate at 100°. It dissolved instantly in cold concentrated sulphuric acid, and was precipitated from the solution on the addition of water. These reactions indicate that the substance is a simple ether, but no probable formula corresponding to the above analytical results, can be assigned to it.

Summary.

The results of this investigation may be briefly summarized as follows:

The monoethyl ether of trimethylene-glycol is readily prepared by the action of sodium and ethyl iodide on the glycol; but it is essential that the glycol be used in considerable excess. The diethyl ether of the glycol has been prepared from the monoethyl ether, but not from the glycol itself, by an exactly similar process.

By the action of phosphorus trichloride, tribromide, and diiodide on the monoethyl ether, the hydroxyl group was replaced by halogen with the production of the ethyl chlor-, brom-, and iod-propyl ethers. The yields obtained were about 50, 75 and 30 per cent. respectively in the three cases. Hydriodic acid gas at 0° caused replacement of the ethoxyl as well as the hydroxyl group.

The diethyl ether of hexamethylene-glycol was found to be produced in very small quantity by the action of sodium on an ethereal solution of ethyl chlorpropyl ether and in somewhat larger quantity by the similar reaction with the corresponding brom and iodo ethers; but the best yields obtained did not exceed 30 per cent. of the theoretical.

By heating the ethyl brompropyl ether in a water-bath for several hours, first with a slight excess of concentrated aqueous potassium cyanide solution, and then with concentrated potash and acidifying, γ-ethoxyvalerianic acid was obtained in a 40 per cent. yield. It was shown that by the electrolysis

of the salt of this acid a small quantity of hexamethylene-glycol diethyl ether is probably formed.

Attempts to prepare a metallic derivative by the action of sodium amalgam and of the zinc-copper couple on the ethyl brompropyl ether were entirely unsuccessful.

The Fittig synthesis was successfully carried out with this bromether and brombenzene, a 54 per cent. yield of ethyl γ-phenylpropyl ether being obtained.

The ethoxypropyl radical was also readily introduced into malonic ether by heating its sodium compound with the ethyl brompropyl ether, the yield being 34 per cent. The substituted malonic ether so obtained gave, on saponification and subsequent heating to 170° of the acid separated from its salt, δ-ethoxyvalerianic acid in a 37 per cent. yield. Another substance was produced in this reaction in considerable quantity, but its nature was not determined.

The following table presents a summary of the boiling-points and specific gravities of all the compounds described for the first time in this article. The boiling-points are those corresponding to the ordinary atmospheric pressure of about 760 mm., except when otherwise indicated. The specific gravities refer to 25° unless otherwise indicated, the water being measured at the same temperature.

Substance.	Boiling-point.	Specific gravity.
$C_2H_5O.CH_2.CH_2.CH_2OH$.	160°–161°.	0.915
$C_2H_5O.CH_2.CH_2.CH_2.OC_2H_5$.	140°–141°.	0.835
$C_2H_5O.CH_2.CH_2.CH_2Cl$.	130°–131°.	0.957
$C_2H_5O.CH_2.CH_2.CH_2Br$.	150°–151°.	1.300
$C_2H_5O.CH_2.CH_2.CH_2I$.	130°–134° (at 150 mm.)	1.585
$C_2H_5O.(CH_2)_4.OC_2H_5$. 208°;	160°–162° (at 200 mm.)	0.845
$C_2H_5O.(CH_2)_4.COOH$.	252°	0.994
$C_2H_5O.(CH_2)_3.CH(CO_2C_2H_5)_2$.	273°	1.016[1]
$C_6H_5.(CH_2)_3.OC_2H_5$.	224°	0.924[1]

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS., MAY, 1897.

[1] At 15°.

ON THE CHLORONITRIDES OF PHOSPHORUS. (II).[1]

By H. N. Stokes.

In a former article[2] I have shown that in addition to the phosphonitrilic chloride,[3] $P_3N_3Cl_6$, discovered by Liebig, there exists another, $P_4N_4Cl_8$, of similar properties, which is formed at the same time, but in smaller quantity. The opinion was expressed that these bodies belong to a series of polymers, $(PNCl_2)_n$, the existence of other members of which was indicated by the formation, in small amount, of a liquid of the same empirical composition.[4] The yield of this secondary product, only 2 per cent. of the theoretical or 1 per cent. of the pentachloride used, was too small to allow of its preparation in quantities large enough to admit of the isolation of its supposed constituents, but a fractional distillation of the few grams at my disposal showed that it contained crystalline substances of higher boiling-points than those of the two bodies thus far known.

The method of preparation then employed consisted in distilling phosphorus pentachloride with a large excess of ammonium chloride in a retort, at atmospheric pressure; it offered but little prospect of obtaining the higher members. The total yield of phosphonitrilic chloride was but 15 per cent. of the theoretical, most of the pentachloride being converted into "phospham" by the excess of ammonium chloride, while only those members could be obtained which distil unchanged at atmospheric pressure. Decreasing the amount of ammonium chloride resulted only in a loss of pentachloride by volatilization, without increasing the yield of the bodies sought after.

The following method has been found to give entirely satisfactory results; several new bodies have been obtained, and the simpler phosphonitrilic chlorides, at least, are now easily accessible substances: If equal molecular weights of phosphorus pentachloride and ammonium chloride be heated in a

[1] Published by permission of the Director of the United States Geological Survey.

[2] This Journal, **17**, 275 (1895): Ber. d. chem. Ges., **28**, 437.

[3] I propose in future to use the term *phosphorus chloronitride* to denote any body composed of phosphorus, nitrogen, and chlorine, the name *phosphonitrilic chloride* being reserved for chloronitrides belonging to the series $(PNCl_2)_n$.

[4] This Journal, **17**, 277, 280, 290.

sealed tube, there results a mixture of chloronitrides, which is partly crystalline and soluble in gasoline, but for the greater part liquid and insoluble in this solvent, and of a high degree of complexity. This may be distilled almost without residue, the distillate being a crystalline mass, impregnated with an oil, and composed almost wholly of a mixture of members of the series $(PNCl_2)_n$ in nearly theoretical amount, containing about 50 per cent. $P_3N_3Cl_6$, and 25 per cent. $P_4N_4Cl_8$, the remainder consisting of the higher homologues. From this distillate the new bodies, with one exception, have been isolated.

The series, as at present known, consists of the following:[1]

	Melting-point.	Boiling-point. 13 mm.	760 mm.
Triphosphonitrilic chloride, $(PNCl_2)_3$	114°	127°	256.5°[2]
Tetraphosphonitrilic chloride, $(PNCl_2)_4$	123.5°	188°	328.5°[3]
Pentaphosphonitrilic chloride, $(PNCl_2)_5$	40.5–41°	223–224.3°	Polymerizes
Hexaphosphonitrilic chloride, $(PNCl_2)_6$	91°	261–263°	Polymerizes
Heptaphosphonitrilic chloride, $(PNCl_2)_7$	Liquid at −18°	289–294°	Polymerizes
Polyphosphonitrilic chloride, $(PNCl_2)_x$	Below red heat.	Depolymerizes on distillation.	

There were obtained, further, a liquid residue of the same empirical composition, of a *mean* molecular weight corresponding nearly to $(PNCl_2)_{11}$, and a small amount of a chloronitride, $P_4N_7Cl_9$, not belonging to the above series. The absence of the lower members, $PNCl_2$ and $(PNCl_2)_2$, is remarkable, and theoretically significant. Indications of a trace of a substance more volatile than the compound $(PNCl_2)_3$, and of similar but stronger odor, were observed, but there is no evidence that it consists of one of the missing bodies.

One of the most remarkable properties of the phosphonitrilic chlorides is that each member of the series is converted by heat into the rubber-like *polyphosphonitrilic chloride*, a body, or mixture of bodies, of very high molecular weight, which is highly elastic and insoluble in all neutral solvents, but which swells enormously in benzene, and which, on distilling at a higher temperature, breaks down into a mixture of all the lower members mentioned above, which can then be separated by appropriate means. In this way it is possible to convert any phosphonitrilic chloride quantitatively into any other by

[1] The melting- and boiling-points are corrected.

[2] 183.8° at 100 mm. [3] 242° at 100 mm.

heat and distillation alone. In preparing any desired member, therefore, we are not limited to the quantity obtained from the first reaction product, but may work the residues over and over again until completely converted into the body sought after. With the exception of a few cases, in which the number of members is limited, as the aldehydes and cyanic acids, this series is therefore unique; I know of no other series of inorganic compounds in which this is possible. Polymerization takes place slowly, but perceptibly, at 250°, and is almost instantaneous at 350°, while depolymerization begins at about 350°, and is rapid at a temperature close to incipient red heat. Triphosphonitrilic chloride, $P_3N_3Cl_6$, is the only member which can be distilled in considerable amount at atmospheric pressure without considerable polymerization and even this polymerizes almost completely on long boiling; at 760 mm. pressure the tetra-compound, $P_4N_4Cl_8$, boils at 328°.5, a temperature at which polymerization occurs quite rapidly, but this, as well as the penta-compound, $P_5N_5Cl_{10}$, and the hexa-compound, $P_6N_6Cl_{12}$, can readily be distilled at 13 mm.; the hepta-compound, $P_7N_7Cl_{14}$, suffers marked polymerization on distilling even at this pressure, and its isolation is therefore attended with much loss. Owing to the rapid change at higher temperatures, I have been unable to isolate any of the higher members, which remain as a considerable oily residuum, and there seems to be but little probability of this being effected by any known method, unless by distilling in a nearly absolute vacuum.

The greatest difficulty in the separation of the members is caused by polymerization. It requires but a small amount of polyphosphonitrilic chloride to cause the liquid to thicken or gelatinize, and therefore to be incapable of further distillation, and some of this body is always formed in the course of a prolonged fractioning of the higher members. It was found, however, that this polymer is much more easily attacked by water than the lower members; when signs of polymerization are observed, it is only necessary to interrupt the distillation, and heat the residue for some time with water, when the resulting oil is again in a condition to continue fractioning. The loss in this operation is small, but the tediousness of a

fractional distillation is thereby extraordinarily increased.

It is noteworthy that no regular progression exists in the melting-points of the phosphonitrilic chlorides, and the same is true of their solubility in the ordinary neutral solvents, but the solubility varies in the same sense as the fusibility. Of the members of known molecular weight, the second, tetraphosphonitrilic chloride, is the least soluble and has the highest melting-point, while the corresponding tetrametaphosphimic acid is the least soluble and most stable of the derived acids. With respect to their stability towards water, the new members (polyphosphonitrilic chloride excepted) resemble those already described, being scarcely attacked by prolonged boiling. In ethereal solution, however, there is a perceptible decrease of stability towards water as we rise in the series, a fact already noted with regard to the first two members.[1]

Notwithstanding the high molecular weight of the bodies isolated, no indication of isomers has been observed, although the fractioning was carried out very thoroughly up to 300° at 13 mm.

The investigation will be continued with the object of obtaining the metaphosphimic acids, and, if possible, the two missing lowest members of the phosphonitrilic chloride series; the right of further investigation in this field, however, is *not* reserved.

Experimental Part.

A mixture (which need not be very intimate) of 4 parts perfectly dry phosphorus pentachloride and 1 part ammonium chloride, as required by the equation

$$PCl_5 + NH_4Cl = PNCl_2 + 4HCl,$$

is introduced into an ordinary "bomb" tube, which has previously been drawn out to a neck. It is practicable to fill the tube entirely to the neck, so that the charge for a tube of ordinary dimensions is about 125 grams, yielding 50–55 grams of chloronitrides. After sealing, the length of the neck, exclusive of the rather long capillary, should be about 10 cm. As the mixture liberates 55 per cent. hydrochloric acid, it is necessary to regulate the heating with great care and to open

[1] This JOURNAL, 17, 289.

the tube repeatedly. The temperature of the furnace is allowed to rise to 150°, at which the reaction begins, when the gas is at once shut off, and the tube opened at about 100° (in the furnace!). This operation is repeated several times, the temperature being allowed to rise 1°–2° higher each time. When the evolution of hydrochloric acid has slackened and the contents of the tube are mainly liquid while hot, the temperature may be carried to 200° or higher, until little or no gas is given off. The operation requires care and judgment, but with careful working it is possible to avoid explosions, and to obtain with a four-tube furnace about 200 grams of mixed chloronitrides in sixteen hours.

The contents of the tube, after cooling, generally consist of a buttery mass or of a thick yellow liquid filled with fine prisms and plates; if heated much above 200°, the liquid frequently separates into two layers. The crystals are soluble in gasoline, but the bulk of the product remains as an immiscible oil.

The neck of the tube is now bent down, the tube placed in an inclined combustion furnace, and by cautious heating, finally to incipient redness, the contents are distilled out. There remains in the tube a very voluminous, spongy, black residue of inconsiderable weight, due to unavoidable impurities and to the impossibility of causing complete reaction in the sense of the above equation. The distillate consists of a crystalline mass impregnated with a yellow oil, and contains about 95 per cent. of the theoretical amount of phosphonitrilic chlorides, with some phosphorus pentachloride, the chloronitride $P_4N_3Cl_9$, and other substances of unknown nature. Before proceeding further, it is necessary to remove the pentachloride, and for this purpose the distillate is melted, poured into *cold* water, and the flask heated in the water-bath for about two hours, the liquids being mixed by blowing air through them. The chloronitrides are then allowed to clear under the hot water, and forced out by means of a wash-bottle arrangement; a separatory funnel cannot be used, as the substance solidifies in the neck, and if allowed to solidify under the wash water, it absorbs so much of this as to cause annoyance in the subsequent distillation. Special drying before distilling is unnecessary.

The product is then distilled up to 200° at 13–15 mm., using an Anschütz flask, as the distillate solidifies instantly on cooling. The residue, containing the members $P_5N_5Cl_{10}$ up, is set aside for later systematic fractional distillation.[1] The distillate, about 70 per cent., consists essentially of $P_3N_3Cl_6$ and $P_4N_4Cl_8$, which, if desired, may be easily separated by fractional distillation *in vacuo*, followed by crystallization from benzene. This is more convenient than the method of separating by steam.[2] If it is desired to convert it into the higher members, it is placed in a combustion tube bent down at about 20 cm. from the open end, and which it should not fill more than one-half after melting. This is laid in an inclined combustion furnace and heated to gentle boiling of the contents. It is well to heat the tube somewhat strongly at a short distance above the liquid, as superheating the vapor promotes polymerization. The time required for polymerization varies greatly; pure triphosphonitrilic chloride may require two hours or more; with the above mixture the time is less, and is shorter the higher the boiling-point; it is shortened by adding already gelatinized substance, which causes the liquid to thicken, and may then be but a few minutes; it is also shortened by heating under pressure. Sooner or later the liquid begins to thicken, and finally it is converted into a stiff, transparent mass, with little or no liquid, and generally discolored by traces of organic matter. The tube is then connected with a long-necked receiver, exhausted, and the depolymerization and distillation effected by heating, from the

[1] This residue contains the small amount of $P_4N_7Cl_9$ formed as a secondary product of the original reagents, and as this is apt to cause inconvenience at a later stage by accumulating with the $P_4N_4Cl_{12}$, it is perhaps well to remove as much as possible at this point. For this purpose the residue is allowed to stand for a day or two at the room temperature, and the crystals removed by sucking out under a good vacuum, best in a large Gooch crucible. The filtrate is cooled for a day or two in a refrigerator, and the new crop of crystals separated in the same way, the filtering flask being allowed to stand in the ice-box. The oily filtrate is set aside, and the united crystalline products distilled up to 240° at 13 mm., whereby most of the $P_5N_5Cl_{10}$ passes over. The residue, consisting of $P_4N_4Cl_{12}$, the small amount of $P_4N_7Cl_9$, and the adhering oil is allowed to crystallize in the refrigerator, and the viscous mass is extracted several times with small amounts of gasoline (boiling at 50°-80°). The residue is boiled with benzene, which extracts the $P_4N_7Cl_9$, which crystallizes on concentrating and cooling. The portion dissolved by the gasoline is worked up with the other residues.

This is the method actually employed, but I am not entirely convinced of its necessity, as it is not possible to remove *all* the $P_4N_7Cl_9$ in this way.

[2] This JOURNAL, **17**, 280.

front backward, to incipient redness. This part of the operation proceeds rapidly, as it is only necessary to guard against frothing over, and to ensure complete condensation, the latter being easily effected by having the limb of the tube at least 20 cm. long. 100 grams can be worked up at one time and the tube can be used repeatedly. The residue does not weigh more than a few milligrams. The distillation may also be made at atmospheric pressure, but the yield of higher products is thereby diminished. The distillate, which entirely resembles that first obtained, excepting in containing no phosphorus pentachloride and no $P_4N_4Cl_8$, is distilled as before, the washing being omitted. In this way the whole quantity of material can finally be converted into a mixture of members higher than $P_4N_4Cl_8$.

The united residues boiling above 200° are now submitted to systematic fractional distillation at 13–15 mm., using an Anschütz flask, provided with a "trap," to prevent flowing back. During the first distillation polymerization generally begins when the temperature of the bath has reached 270°, but with later distillations, at a higher temperature, and the higher, the purer the fractions are. When polymerization begins, which is indicated by frothing and thickening, the operation is interrupted and the residue heated in the flask with water in the water-bath until it has completely liquefied, which is assisted by agitation, the oil separated[1] and the distillation continued. It has not been found practicable to continue the distillation at a higher temperature than that obtained by heating the bath to 370°, for the liquid begins to polymerize in a few moments, and but an inconsiderable distillate can be obtained. Moreover, at this temperature the polymer shows signs of breaking down into simpler bodies, and the distillate does not consist only of high-boiling members. The total amount of final residue is not very great, and as shown below consists likewise of phosphonitrilic chlorides of still higher molecular weight. In later distillations from 200° upward, polymerization usually stops the process at 260°–270°, but after appropriate washing, the residue may be

[1] In this case a separatory funnel may be used, as the higher chloronitrides are liquid below 80°.

distilled to a much higher temperature. After 8–10 distillations three main fractions are obtained, which are then worked up separately. As $P_4N_4Cl_{10}$, though crystalline, is extremely soluble, it is necessary to carry out the distillations with the first main fraction until a practically sharp boiling-point is obtained, in which connection it may be noted that at 17–20 mm. a change of 1 mm. pressure causes a change of about 1° in the boiling-point, and at 13 mm. a change of about 2°. $P_7N_7Cl_{14}$, being liquid, must also be isolated by distillation only, but at its boiling-point polymerization is so rapid that great loss ensues during a series of distillations. The final purification of $P_4N_6Cl_{12}$ can be effected by repeated recrystallization from benzene, combined with treatment with gasoline to remove the $P_4N_7Cl_9$, which always accompanies it, having nearly the same boiling-point; a complete separation of these two bodies can scarcely be effected by distillation alone.

Owing to many modifications introduced in developing the above method, no accurate statement of the yield can be given; the final product was about 225 grams $P_4N_4Cl_{10}$, 110 grams $P_4N_4Cl_{12}$, 10 grams $P_7N_7Cl_{14}$, and 5 grams $P_4N_7Cl_9$.

Analytical Methods.—With the exception of polyphosphonitrilic chloride, the chloronitrides were analyzed by decomposing in the following manner:

For *phosphorus*, by warming with alcohol and a little ammonia in a platinum crucible until completely dissolved, evaporating to dryness and heating to fuming for an hour with strong sulphuric acid, the crucible being kept covered.

For *nitrogen*, by treating as above, omitting the ammonia.

For *chlorine*, by heating with alcohol and ammonia. It is necessary to precipitate with silver nitrate in the presence of a large volume of 10 per cent. nitric acid and to filter hot, in order to avoid the formation of silver metaphosphimates, which are difficultly soluble in dilute nitric acid.

In decomposing polyphosphonitrilic chloride, which is attacked by water alone, the alcohol was omitted. The method of Carius was used for determining chlorine, as it was found that otherwise compounds insoluble in dilute nitric acid were

formed. For the other chloronitrides this method offers no advantage.

Molecular weight determinations were made by the boiling-point method with the apparatus of Hite,[1] using as solvent carefully purified and dried benzene.[2]

Pentaphosphonitrilic Chloride, $P_5N_5Cl_{10}$.—This body, carefully purified by fractional distillation, as described above, gave on analysis:

	Calculated for $P_5N_5Cl_{10}$.	Found.
P	26.75	26.87
N	12.11	12.05
Cl	61.14	61.42

Ratio, P : N : Cl = 1 : 0.99 : 2.00.

Molecular Weight. Solvent: Benzene.

Grams solvent.	Grams substance.	Elevation.	Molecular weight found.	Percentage variation from theoretical.
46.49	1.4688	0.137°	619	+6.2
"	2.9439	0.287°	589	+1.6
"	4.4337	0.437°	583	+0.5

Calculated for $P_5N_5Cl_{10}$, 579.8.

Pentaphosphonitrilic chloride fuses at 40°.5–41°, and boils at 223°–224°.3 (corr.) at 13 mm. Its vapor is without the pronounced and characteristic aromatic odor possessed by that of triphosphonitrilic chloride. At its melting-point, it is miscible in all proportions with benzene, gasoline, ether and carbon disulphide, and cannot be recrystallized from any of these solvents; in fact, small fragments liquefy instantly in their concentrated vapors. Glacial acetic acid also dissolves it quite readily, and from this solution water throws it out as an oil, solidifying at once on touching. It shows a decided tendency to superfusion, especially when not absolutely pure; when left by evaporating its ether or benzene solution, it may remain liquid for days, but solidifies at once on touching with a glass rod, usually to a decidedly crystalline mass, at other times to a transparent glass. The pure substance, when

[1] This JOURNAL, **17**, 512.

[2] The molecular weight of $P_3N_3Cl_6$ has been determined by the vapor density method (J. Chem. Soc., [2], **2**, 225; This JOURNAL, **17**, 283.) A series of determinations by the boiling-point method gave 346, 350, 353. Calculated 347.9.

fused, slowly solidifies, long, flat crystals shooting out through the liquid, which are limited only by the size of the vessel, crystals of 10 cm. in length being readily obtained. It contracts greatly on solidifying. When pure, the solidified mass is naturally dry, but the least contamination with other members of the series causes a portion to remain liquid, which is easily detected by crushing on a piece of filter-paper; this is a very good test of its purity. This tendency to superfusion must be borne in mind in separating it by fractional distillation; a nearly pure sample will remain liquid much longer than the higher or lower fractions. In ether solution it is perceptibly more easily attacked by water than the preceding chloronitride, but hot water alone is almost without action.

Hexaphosphonitrilic Chloride, $P_6N_6Cl_{12}$. — After repeated crystallization from benzene,[1] this gave:

	Calculated for $P_6N_6Cl_{12}$.	Found.
P	26.75	26.98
N	12.11	12.37
Cl	61.14	60.98

Ratio, P : N : Cl = 1 : 1.01 : 1.98.

Molecular Weight. Solvent: Benzene.

Grams solvent.	Grams substance.	Elevation.	Molecular weight.	Percentage variation from theoretical.
47.12	1.8058	0.152°	673	−3.2
"	3.6190	0.293°	700	+0.6
45.72	1.0101	0.083°	711	+2.1
"	4.4898	0.365°	718	+3.2
"	8.0070	0.664°	704	+1.2

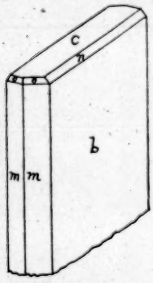
Calculated for $P_6N_6Cl_{12}$, 695.8.

Hexaphosphonitrilic chloride fuses at 91° (corr.), and boils at 261°–263° (corr.) at 13 mm., and at 281°–282° (corr.) at 26 mm. It may be recrystallized from benzene, in which, however, it is more soluble than triphosphonitrilic chloride; ether, gasoline, and carbon disulphide also dissolve it readily; in alcohol it dissolves somewhat slowly with decomposition. It shows no tendency to superfusion. It crystallizes well, in

[1] A contamination with $P_6N_7Cl_9$ may be detected by treatment with gasoline, when the much smaller crystals of the latter are seen to dissolve much more slowly.

rather large crystals, which were examined by Mr. Wirt Tassin, to whom I am indebted for the following statement:

"$P_6N_6Cl_{12}$ crystallizes in the orthorhombic system in long, prismatic crystals, showing the following forms: *c* (001), *b* (010), *m* (110), *o* (111), *n* (011). Of these *c* is the dominant form; *b* large and well developed; *m* fair, though usually narrow, and *o* and *n* small and usually in similar development. *c*, *b*, *m*, *o* is the combination occurring most frequently; less often *c*, *b*, *m*, *n*, *o*; and rarely *c*, *b*, *m*. Angles *m* : *m* 57° 28′, *b* : *m* 61° 16′, *b* : *n* 40° 23′, *n* : *c* 49° 37′. Axial ratio *a* : *b* : *c* = 0.54824 : 1 : 1.17568. The crystals are optically positive. Plane of the optic axes (100); colorless to white; transparent; and have a perfect basal cleavage."



It is scarcely attacked by boiling water, but if kept in moist air it very slowly evolves hydrochloric acid. Its ether solution, shaken with water, slowly gives a metaphosphimic acid; syrupy chlorhydrines are formed as intermediate products.

Heptaphosphonitrilic Chloride, $P_7N_7Cl_{14}$.—After many distillations, this gave:

	Calculated for $P_7N_7Cl_{14}$.	Found.
P	26.75	26.57
N	12.11	12.12
Cl	61.14	61.28

Ratio P : N : Cl = 1 : 1.01 : 2.02.

Molecular Weight. Solvent: Benzene.

Grams solvent.	Grams substance.	Elevation.	Molecular weight.	Percentage variation from theoretical.
47.09	3.5621	0.250°	808	—0.5
"	7.3979	0.523°	802	—1.2

Calculated for $P_7N_7Cl_{14}$, 811.7.

Heptaphosphonitrilic chloride is a nearly colorless, rather viscous liquid, which does not solidify at —18°, and which boils at 289°–294° (corr.) at 13 mm., undergoing some polymerization. It is readily miscible with benzene, gasoline and

ether, and towards water shows the stability manifested by the preceding chloronitrides.

Residual Oily Phosphonitrilic Chlorides.[1]—The residue which did not distil at 13 mm. when the temperature of the bath was 370°, was boiled with water to remove the solid polyphosphonitrilic chloride, filtered, and carefully dried *in vacuo* over sulphuric acid. It is a thick liquid which gave on analysis :

	Calculated for $(PNCl_2)_x$.	Found.
P	26.75	26.79
N	12.11	12.39
Cl	61.14	62.00

Ratio, P : N : Cl = 1 : 1.02 : 2.02.

Although the oil is doubtless a mixture, the above figures show that the constituents are members of the series $(PNCl_2)_n$. A determination of *the mean molecular weight* was made, with the following results :

Grams solvent.	Grams substance.	Elevation.	Molecular weight.
46.72	4.130	0.178°	1326
"	7.853	0.348°	1290

Mean 1308. This does not lie far from that required by the formula $P_{11}N_{11}Cl_{22}$ (calculated, 1276). This result is interesting in as far as it shows that a phosphonitrilic chloride of this molecular weight may exist, that it is stable and miscible with benzene, gasoline and ether, and that the molecular weight of the solid polymer described below, which is insoluble, is probably very much higher. The oil has a reddish brown color, due to dissolved impurities, which are destroyed by heating with strong nitric acid. It cannot be distilled even at 13 mm., as it polymerizes almost instantly. In its behavior towards water, it resembles the preceding members of the series.

Polyphosphonitrilic Chloride, $(PNCl_2)_x$.—This remarkable body, frequently alluded to above, is formed when any of the lower members are heated, slowly at 250°, and very rapidly at 350°. As the change is reversible, *complete* transformation

[1] It is unlikely that these consist entirely of the original depolymerization products ; a portion is doubtless formed by polymerization during distillation.

cannot be effected, but reaches perhaps 90 per cent., the remainder consisting not only of the original phosphonitrilic chloride, but of others. These can be extracted by anhydrous benzene. The sample, the analysis of which is given, was prepared by heating pure triphosphonitrilic chloride in a sealed tube at 350°–360°. The transparent elastic product was repeatedly extracted with benzene dried over sodium and the absorbed benzene removed in a vacuum with constant exhaustion over paraffin, and finally by heating *in vacuo* at 110°. Analysis gave:

	Calculated for $(PNCl_2)_x$.	Found.
P	26.75	26.78
N	12.11	12.27
Cl	61.14	60.45

Ratio, P : N : Cl = 1 : 1.01 : 1.98.

Polyphosphonitrilic chloride, when perfectly pure, is colorless and transparent, but is generally somewhat discolored by traces of organic matter. Its most striking property is its elasticity. It may be drawn out like rubber, and shows even a greater tendency to rebound from hard surfaces. It is readily cut with the shears. It is insoluble in all neutral solvents, but absorbs benzene, swelling to many times its original volume and forming a jelly of but little coherence; on evaporating the benzene it returns to its original condition; ether is absorbed, but less readily, and other chloronitrides are taken up in a similar manner. Hot water slowly dissolves it with decomposition; in warm dilute ammonia it swells, gelatinizes and finally dissolves; hot caustic soda does not dissolve it readily, apparently insoluble sodium salts being formed. It begins to depolymerize towards 350°, and this change is rapid just below red heat, and is accompanied by partial fusion, the products being, as described above, a mixture of lower phosphonitrilic chlorides. These transformations are not modified by heating in an atmosphere of hydrochloric acid. When perfectly pure, it leaves no residue whatever on distilling. No difference could be detected in the product formed from different phosphonitrilic chlorides.

Nitrilo-hexaphosphonitrilic Chloride, $P_6N_7Cl_9$.—The separa-

tion of this chloronitride, which does not belong to the phosphonitrilic chloride series, is described above. After four crystallizations from benzene, it gave:

	Calculated for $P_4N_7Cl_9$.	Found.
P	30.84	30.74
N	16.29	16.29
Cl	52.87	53.01

A molecular weight determination, kindly made for me by Dr. H. C. Jones, of the Johns Hopkins University, with a limited quantity of material, in benzene solution, gave 667; calculated for $P_4N_7Cl_9$, 603.5. This, with the analysis, suffices to establish the above molecular formula.

Nitrilo-hexaphosphonitrilic chloride strikingly resembles the phosphonitrilic chlorides. It fuses at 237°.5 (corr.) and boils at 251°–261° (corr.) at 13 mm. without change. The boiling-point coincides closely with that of hexaphosphonitrilic chloride (261°–263° corr. at 13 mm.), hence it is found associated with the latter. Heated in small quantities on foil, it volatilizes without residue, but at a higher temperature in a sealed tube it undergoes a change the exact nature of which has not been determined, but which involves the formation of a substance resembling polyphosphonitrilic chloride, which yields lower phosphonitrilic chlorides on distilling. It crystallizes in transparent prisms of not more than 1 mm. in length, apparently rhombic, which are often united to acicular forms. When pulverized it becomes electrified. It dissolves in about 20 parts cold and 5 parts boiling benzene,[1] is more soluble in carbon disulphide, but less soluble in gasoline and in ether. Towards water it is nearly as stable as hexaphosphonitrilic chloride, but is slowly attacked when exposed to atmospheric moisture. Hot dilute ammonia dissolves it very slowly, but more rapidly when alcohol is added.

This body is obviously a secondary product of the reaction of phosphorus pentachloride and ammonium chloride, as it is never found when a pure phosphonitrilic chloride is polymerized and depolymerized. It is noteworthy that no indication of other bodies of a similar nature has been observed, although no reason appears why they should not be formed at the same

[1] Approximate only.

time. Whether it is in reality hexaphosphonitrilic chloride in which three chlorine atoms are replaced by one of nitrogen or not, cannot be decided at present.

U. S. GEOLOGICAL SURVEY, WASHINGTON, D. C.,
JULY, 1897.

Contributions from the Chemical Laboratory of the Case School of Applied Science.

XXVIII.—PRELIMINARY PAPER ON THE COMPOSITION OF CALIFORNIA PETROLEUM.

BY CHARLES F. MABERY.

During the last four years I have been extremely desirous of undertaking an examination of California petroleum, and have made several attempts to procure specimens of the crude oil. But all attempts to procure authentic material failed for a long time, and my time was so fully occupied with oils from other fields, with an adequate supply at hand, that I could scarcely have found time to devote to it. Last February Professor Peckham informed me that he hoped to make arrangements to continue his study of the California products in the direction of determining their composition. Although I had then recently been informed that a quantity of crude oil from the Ventura County field had been shipped to me, I gladly offered Professor Peckham any facilities in my laboratory he might need for prosecuting this work. Subsequently I learned that a change in his plans would not permit of his carrying out his intention, and he informed me that I was at liberty to proceed on my own plans. Having received another specimen of crude oil from Fresno County I undertook the work with vigor. While there is still much to be done on the higher vacuum distillates, it has seemed best at this stage to give an account of what has been accomplished.

In the extremely interesting account which Peckham gave in "The Production of Petroleum" by the late Joseph D. Weeks in 1894, of the occurrence and technology of California petroleum, it appears that the production of crude oil in 1894 from all sources amounted to 683,000 barrels. On account of the peculiar occurrence of oil in these fields, and the properties of the crude oils, which differ within very wide limits between the most volatile Pennsylvania crude oil, and

the heaviest products next to asphalt, these oils possess an extreme interest not inferior to that of any American petroleum. I hope to include in this examination a sufficient range of crude oils from different fields to be able to demonstrate the composition of the typical specimens.

The oils I have received are so different in their properties that they may be accepted as extremes in a series of widely varying products. One specimen from Ventura County is extremely heavy, small proportions distilling below 150°; the other from Fresno County is much lighter, and it distils in very large proportions below 150°, leaving comparatively small amounts above 250°.

Ventura County Petroleum.

The peculiar occurrence of oil in the Ventura County field where it is found in the strata of shales at shallow depths, never greater than 117 feet, or in places as the heavier maltha, has been fully described by Peckham, and accounts of these products are also given by Redwood and other authors of works on petroleum. The specimen which I received was very thick and dark, nearly black, slightly brownish in transmitted light. A determination of its specific gravity at 20° gave 0.8882. It is a high sulphur oil, as shown by a combustion which gave 0.84 per cent. It is also one of the California oils which contain a high percentage of nitrogen compounds; a determination by the Kjeldahl method gave 0.53 per cent. It showed a larger capacity for the absorption of bromine than Pennsylvania or Ohio oils, but approximately the same as that of Canadian oil from Oil Springs. Its bromine-absorption was found to be 17.72 per cent. It is quite probable that a considerable proportion of the bromine disappeared by substitution, since evidently the crude oil contains large quantities of the aromatic hydrocarbons. A combustion of the crude oil gave 85.60 per cent. of carbon, and 12.84 per cent. of hydrogen. The proportion of oxygen compounds would therefore seem to be quite small.

A distillation of the crude oil under atmospheric pressure gave 9.7 per cent. below 150°, 29.1 per cent. between 150° and 300°, and 61.2 per cent. of residue above 300°. The specific

gravity and bromine-absorption of the distillates are given in the following table:

	Br-Absorption.	Specific gravity.
−150°	5.6	0.7395 at 20°.
150°–200°	6.0	0.7823 " "
206°–250°	9.17	0.8252 " "
250°–300°	18.15	0.7591 " "
−300°	....	0.9528 " 45°.

The first distillate began to appear at 60°, but small amounts came over below 150°. All portions were colorless below 250°; at this point a yellow color appeared with an odor of decomposition. The higher distillates became dark yellow on standing and gave more odor of decomposition. The residue above 300° was a thick, nearly solid, tar, and its high specific gravity with the large proportion remaining above 300° explains in part the difficulty that has been encountered in preparing burning oil from Ventura County petroleum. In the distillation under atmospheric pressure, cracking began at 350°; while the distillate above was somewhat decomposed, these higher portions appear to be quite stable.

For the separation of constituents with higher boiling-points 20 liters was distilled under atmospheric pressure to 150°, then the distillation was continued *in vacuo* under a tension of 50 mm. to 275°. The following weights were obtained within limits of 25°; the specific gravity determinations were made on a Westphal balance:

Atmospheric pressure.	Weight in grams.	Specific gravity at 20°.
−150°	850	0.7269
−100°	605	0.7342
100°–125°	1000	0.7452
125°–150°	1050	0.7689
150°–175°	1115	0.8212
175°–200°	1110	0.8432
200°–225°	1025	0.8618
225°–250°	1565	0.8824
250°–300°	1005	0.9071

The next distillation in vacuum was made within 5°, but the results of subsequent work on these portions will be presented in another paper.

None of the vacuum distillates nor the residue showed the

slightest indication of decomposition; all portions had the natural odor of the constituents of the crude oil. The fraction 250°–275° when cooled with salt and ice became nearly solid from the separation of paraffin, but from the next lower fraction scarcely any paraffin separated.

To ascertain whether the series C_nH_{2n+2} forms the main body of this petroleum below 200°, distillation under atmospheric pressure of the lower portions was continued until the constituents collected within the limits of their characteristic boiling-points. After the sixth distillation 20 grams collected at 78°–84°, which was shown to contain a large proportion of benzol by the formation of nitrobenzol. The formation of nitrotoluol in the fractions 108°–112° showed the presence of toluol. Approximately 25 grams collected at 97°–100° which gave as its specific gravity 0.7341 at 20°, a value much higher than the specific gravity of the heptane from Pennsylvania petroleum, 0.7184 at 15° (Warren), but approaching the specific gravity of the distillate 95°–100° separated by Beilstein and Kurbatoff from Russian petroleum, 0.748. A portion of this distillate was agitated thoroughly with a mixture of nitric and sulphuric acids, and boiled with sodium until the nitro-product in solution was completely decomposed, and again distilled. Its specific gravity was then 0.7268, considerably higher than the specific gravity found by Warren in the corresponding distillates from Pennsylvania oil after treating with concentrated nitric acid, 0.7048, but approximately the same as Beilstein and Kurbatoff found in the Russian distillate after treating with fuming sulphuric acid, 0.733. A combustion of this fraction gave the following percentages of carbon and hydrogen:

0.1575 gram of the oil gave 0.4950 gram CO_2 and 0.1995 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.70
H	14.29	14.08

The composition was not changed by purification, an analysis giving:

C	85.60
H	14.28

The oil which separated after treatment with the mixture of acids soon became solid and partially crystallized in long, slender needles. It will be further examined. The high specific gravity of this product and the proportions of carbon and hydrogen would seem to indicate heptanaphthene.

At 117°–119°, after the seventh distillation, 35 grams collected that gave as its specific gravity, 0.7489 at 20°. The following percentages of carbon and hydrogen were obtained by analysis:

0.1568 gram of the oil gave 0.4920 gram CO_2 and 0.1958 gram H_2O.

C	85.59
H	13.87

Upon treating a portion of this distillate with nitric and sulphuric acids a light yellow oil heavier than water separated that was doubtless nitroxylol. The remaining oil was boiled a long time with sodium, agitated with fuming sulphuric acid, washed with sodic hydrate, dried and again distilled. Analysis of the purified oil gave the following results:

0.1606 gram of the oil gave 0.5037 gram CO_2 and 0.1996 gram H_2O.

	Calculated for C_nH_{2n}.	Calculated for C_nH_{2n+2}.	Found.
C	85.71	84.20	85.55
H	14.29	15.79	13.81

Specific gravity of the purified oil, 0.7405. Even after the vigorous means of purification to which this distillate was subjected it showed no change in its composition. The specific gravity of petroleum octane boiling at 119.°5, is 0.7100; of octonaphthene which Beilstein and Kurbatoff separated from Russian oil, after purification with nitric and sulphuric acids, 0.7582 at 17.°5.

The high specific gravity, and the proportions of carbon and hydrogen, suggest the possibility that this body from the California oil may be octonaphthene.

45 grams of an oil collected at 123°–125°, that gave as its specific gravity at 20°, 0.7553. The following composition was shown by analysis:

0.1574 gram of the oil gave 0.4935 gram CO_2, and 0.1975 gram H_2O.

C	85.49
H	13.91

After thorough treatment with nitric and sulphuric acids and boiling with sodium, the specific gravity of this oil was reduced to 0.7424, and a combustion gave the following percentages of carbon and hydrogen :

0.1507 gram of the oil gave 0.4720 gram CO_2, and 0.1946 gram H_2O.

	Calculated for C_8H_{18}.	C_nH_{2n}.	Found.
C	84.20	85.71	85.43
H	15.79	14.28	14.33

These values are sufficient to exclude normal octane in any considerable quantity from this oil. If this hydrocarbon is not present, further distillation should separate this fraction into lower and higher constituents.

No further attention was given to the portions between 125° and 155°. At 159°–160°, after the eleventh distillation 30 grams came together, which gave as its specific gravity 0.7898. A combustion gave the following percentages of carbon and hydrogen :

0.1680 gram of the oil gave 0.5257 gram CO_2, and 0.2109 gram H_2O.

C	85.35
H	13.95

After treatment with the acid mixture and sodium the composition was scarcely changed.

0.1652 gram of the oil gave 0.5174 gram CO_2, and 0.2086 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.40
H	14.29	14.04

Markownikoff found the specific gravity of dekanaphthene, boiling-point, 160–165, to be 0.783 at 15°.

At the end of the seventeenth distillation, 50 grams collected at 169°–172°, with a specific gravity 0.7987 at 20°. A combustion gave the following percentages of carbon and hydrogen :

0.1614 gram of the oil gave 0.5051 gram CO_2 and 0.2046 gram H_2O.

C	85.35
H	14.09

Agitation of this fraction with the acid mixture caused the separation of a nitro-product heavier than water. It required long continued action of sodium to remove entirely the nitro-derivative. After redistillation the remaining oil was unchanged on long standing with sodium. Its composition was hardly changed by the action of the acids.

0.1670 gram of the oil gave 0.5090 gram CO_2, and 0.2046 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.69
H	14.29	14.21

A determination of the specific gravity of the purified oil at 20° gave 0.7733.

The distillation of the higher portions was not carried far enough for a separation of their individual constituents.

The presence in this petroleum of a constituent with a boiling-point in the vicinity of 170°, the boiling-point of the decane in Pennsylvania petroleum, is a peculiar coincidence. After seventeen distillations it would seem that any mixture should separate into its constituents. (In the vicinity of 180° very little distillate collected. The treatment with acids should have been sufficient to remove the cymols.)

The high specific gravity of the distillates 97°–100°, 117°–119°, 159°–160°, 169°–170°, with the percentage composition supporting the series C_nH_{2n}, indicates the naphthenes. These bodies evidently require further study.

Fresno County Petroleum.

As explained above, this oil differs very materially in its properties from the Ventura County product. It is lighter in color and has more of a greenish hue. Its lower specific gravity at 20°, 0.8423 indicates more of the volatile constituents. A combustion gave the following percentages of carbon and hydrogen: Carbon, 86.24; hydrogen, 13.08. It is not a high sulphur oil, as shown by a combustion, which gave 0.21 per cent. of sulphur. A determination of sulphur by the

Kjeldahl method gave I, 0.10; II, 0.12 per cent. The bromine-absorption of the crude oil gave 9.07 per cent., considerably less than that of the Ventura County oil.

Under atmospheric pressure this oil distilled in the following proportions:

	Per cent.
−150°	33.06
150°–200°	24.79
200°–250°	20.66
250°–300°	12.40
Residue	9.09

All these distillates were colorless below 250°. Determinations of bromine-absorption and specific gravity gave the following results:

	Bromine-absorption.	Specific gravity at 20°.
−150°	17.21	0.7829
150°–200°	14.23	0.8268
200°–250°	32.10	0.8725
250°–300°	21.68	0.9090
+300°		0.9356

The absorption of bromine by these fractions is very much greater than by the corresponding fractions from Ventura County oil. This cannot be due to cracking, since, although the difference is greater in the distillate 200°–250°, it is large in the distillate below 150°. Similar differences are observed in the specific gravity of the distillates; those from the Fresno County oil are much higher than those from the Ventura oil.

When distilled *in vacuo*, 10 liters of the Fresno County oil gave the following weights:

	Weight in grams.
−150° (at. pres.)	2090
−100° (50 mm.)	1165
100°–125°	970
125°–150°	1445
150°–175°	935
175°–200°	595
200°–225°	330
Residue	2470

The distillation of these fractions is now in progress within narrower limits of temperature.

Aid in the work described in this paper was given by the

American Academy of Arts and Sciences from the C. M. Warren fund for chemical research. I have been aided in the experimental details by Mr. P. M. Shaw, who selected a portion of this work as the subject of a thesis for the degree of Bachelor of Science, and by Mr. Edward J. Hudson, who will continue with me the study of California petroleum.

ON THE SOLUBILITY OF AMMONIA IN WATER AT TEMPERATURES BELOW 0° C.

By J. W. Mallet.

Roscoe and Dittmar's table[1] of the solubility of ammonia in water at different temperatures, under normal pressure, begins at 0° C., and there seem to be no recorded measurements of solubility at any lower temperatures. It is stated on the authority of Fourcroy and Vanquelin[2] that a "concentrated" aqueous solution of ammonia—the exact amount in solution not given; probably not determined—does not freeze till cooled to between —38° and —41°, that it then forms brilliant flexible needles, and that at —49° it solidifies to a gray gelatinous mass, almost destitute of odor.

It seemed interesting to try the effect of continuing to pass gaseous ammonia into an already strong aqueous solution at temperatures much below zero, and particularly to see whether any visible change of behavior would mark the presence of enough ammonia to represent the hydroxide of ammonium, often assumed to exist in the ordinary solution, but without any surplus water. The proportion in question—one molecule of ammonia for one of water, might, from an inspection of Roscoe and Dittmar's table, be expected to occur at a temperature but little below zero. Taking advantage of a fall of finely pulverulent dry snow, followed by two or three days of cold weather, during which the atmospheric temperature was about —8° to —12° C., the following experiments were made last winter. In anticipation of such an opportunity, the apparatus had been made ready some time before.

A strong solution of ammonia in water was placed in a bu-

[1] J. Chem. Soc., **12**, 128—quoted in Roscoe and Schorlemmer's Treatise on Chemistry, **1**, 385.

[2] L. Gmelin's Handbook of Chemistry (Cavendish Soc. transl.) **2**, 425.

rette-like glass tube of the form shown in Fig. 1, of which the larger cylindrical part was about 220 mm. long and 25 mm. in internal diameter, the narrow tube below about 100 mm. long and only about 1 mm. in internal diameter, with a small glass stop-cock about 30 mm. above the orifice. The cylinder was graduated for about two-thirds of its length into cubic centimeters. By means of an india-rubber stopper, perforated to grasp tightly the narrow tube, and then cut in two in the line of its axis, this part of the burette was fixed in the neck of an inverted gas-jar, the body of which was about 180 mm. high, with an internal diameter of about 120 mm., so that the cylindrical body of the burette could be surrounded by a freezing-mixture contained in the jar, without any leakage occurring at the neck, the narrow—almost capillary—tube and stop-cock being below and outside the jar. The open mouth of the burette above was loosely closed by a doubly-perforated stopper, through which passed a small tube for the introduction of ammonia gas, and an alcohol thermometer, each fitting so as to be easily slid up or down. The thermometer was carefully made by Mr. Henry J. Green, of Brooklyn, N. Y., contained pure (uncolored) alcohol, was graduated on the glass stem, and had the (centigrade) scale verified by comparison with a (Fahrenheit) mercurial thermometer, itself tested by comparison with a gas thermometer, at the following points; $+32°$, $+12°$, $-8°$, and $-28°$ F. The gaseous ammonia was obtained by simply heating in a flask the strong aqueous solution. There was, of course, no need for drying it, but it was cooled, and incidentally in large measure dried, by passing it first through an empty flask surrounded by snow, and then through a spiral coil of glass tubing immersed in a bath of snow and common salt. Thence by an india-rubber connecting tube it passed into the already strong solution in water contained in the burette. This was surrounded in the jar by a freezing-mixture of snow and commercial hydrochloric acid, both materials having been separately cooled down in advance by snow and salt. In consequence of the evolution of heat as more ammonia was absorbed by the water in the

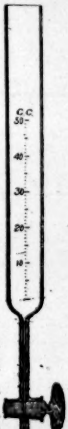


FIG. 1.

burette, it became necessary to allow ample time for cooling down again, and to renew the freezing-mixture in the jar, drawing off the old mixture by means of a specially arranged and rapidly acting siphon. In order to get the lowest temperature reached (between —45° and —46° C.) it was necessary to doubly cool the last portions of snow and hydrochloric acid, first by snow and salt, and then by separate exposure to some of the already cooled snow and hydrochloric acid mixture. The passage of the gas into the solution was continued until it went through very freely unabsorbed. The liquid in the burette continually increased in volume, so that, when samples were drawn off by the stop-cock, enough was first run off to effectually cool the projecting part of the narrow tube and the stop-cock itself, and to bring the level of the remaining liquid down to one of the graduation marks, from which a measured sample might then be taken off. A number of light glass flasks, each of about 300 cc. capacity, furnished with stoppers, were in advance about three-fourths filled with water and severally weighed with accuracy on a good analytical balance. These flasks of water were brought down to o° C. by immersion in snow, and—operating out of doors—the several samples of liquid ammonia were run into them from the burette, producing at once such large dilution that there was no further fear of loss of ammonia by standing over, with the stoppers inserted, until the flasks could be reweighed—the gain of weight in each case representing the amount of liquid taken from the burette—and the amount of real ammonia determined by neutralization with a standard solution of sulphuric acid. The first sample was taken at —40° C., and then, by simply removing the freezing-mixture of snow and hydrochloric acid from the jar, the temperature of the liquid in the burette was allowed to slowly rise, and as the thermometer marked different desired points it was raised for a moment out of the liquid, another sample drawn off into the water in one of the flasks beneath, and the thermometer lowered again. One or two fairly good measurements of the volumes of the samples were made, but, owing to the necessity for quick work, and the difficulty of seeing satisfactorily through the

dimmed surface of the glass, most of these measurements were little to be relied on.

The following results were obtained, so expressed as to form a continuation of Roscoe and Dittmar's table. The atmospheric pressure at the time was 743–744.5 mm., corrected for temperature of the mercurial column.

At —10° C. 1 gram of water dissolved 1.115 grams of ammonia.

At —20° C. 1 gram of water dissolved 1.768 grams of ammonia.

At —30° C. 1 gram of water dissolved 2.781 grams of ammonia.

At —40° C. 1 gram of water dissolved 2.946 grams of ammonia.

The taking up of enough ammonia to form ammonium hydroxide was not attended with any apparent change of behavior, and continuous liquefaction went on smoothly to the lowest temperature reached, with no separation of any solid product. After the freezing-mixture had been withdrawn the temperature rose at first very gradually in consequence of rapid surface evaporation of ammonia. At —25° C. (barometer at 743.4 mm. (corr.)) steady, but not tumultuous ebullition took place and continued for several minutes. A sample taken at this point had the composition: 1 gram of water and 2.554 grams of ammonia.

By interpolation from Regnault's results, the tension of the vapor from liquefied ammonia at —25°.6 C. would be about 1167 mm.

A sample was also taken at —3°.9, which proved to consist of 1 gram of water and 0.947 gram of ammonia—this last corresponding almost exactly with the calculated proportion for ammonium hydroxide, and agreeing also quite closely with an extension of Roscoe and Dittmar's table to the temperature named, allowance being made for the pressure being a little below normal.

These results are graphically plotted in Fig. 2, which includes also the determinations of Roscoe and Dittmar for +40° to 0°. It will be seen that the curve changes rapidly a little below the temperature corresponding to the formation of

$(NH_4)OH$, and the amount of ammonia absorbed is much

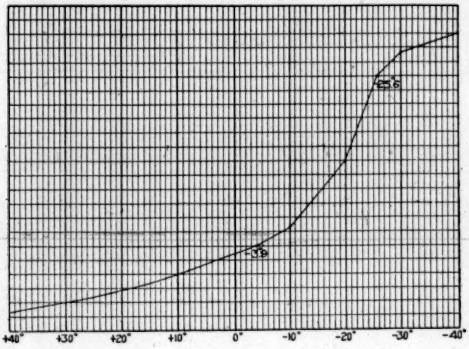


Fig. 2.

greater than would be called for by an extension of Roscoe and Dittmar's numbers.

As regards the reversal of curvature before —30° is reached, some allowance must doubtless be made for loss of ammonia by the samples drawn at the lowest temperatures in dropping through the air into the ice-water in the flasks in spite of the precautions taken to minimize loss from this source. And, in view of the fact that liquefied ammonia boils at —33°.7 under a pressure of 749.3 mm. (Bunsen), the amount of ammonia found in the contents of the burette below this point would, of course, go on increasing indefinitely, depending simply on the length of time allowed for condensation and the more or less free supply of the gas. It appears that ammonium hydroxide, if such a substance exist, or the solution of ammonia in water in proportion corresponding to such a compound, continues to dissolve gaseous ammonia, or mixes with liquefied ammonia, down to and beyond the normal boiling-point of the latter, but the proportion dissolved is much greater than would be called for by an extension of the curve representing solubility at temperatures above 0°.

As has been stated, measurement of the volumes of the

samples taken could not be very satisfactorily carried out. It may be mentioned, however, that a comparison of volume with weight gave for the liquid at —30° a density of about 0.718, and for that at —40° about 0.731, as referred to water at +4°. The latter figure being greater than the former may probably be accounted for by the very high value of the coefficient of dilatation for liquefied gases. Calculating from Jolly's results, the density of liquefied ammonia itself at —40° ought to be something like 0.673.

UNIVERSITY OF VIRGINIA,
August 30, 1897.

NOTE ON A SOMEWHAT REMARKABLE CASE OF THE RAPID POLYMERIZATION OF CHLORAL.

BY J. W. MALLET.

A specimen of anhydrous chloral—trichloracetaldehyde—of about 250 grams was contained in a glass vial of a form commonly used in Germany, with small drawn-out neck, hermetically sealed. It had been on hand for more than a year, and had originally been quite clear, but doubtless not absolutely pure, very likely containing traces of sulphuric acid, as a few small white flocks of the polymeric meta-chloral had begun to show at the bottom.

This specimen, with a number of others, had been exhibited on the lecture-table, handled by several persons, and moved back to the collection room whence it had come. It was placed temporarily on a table, among other bottles, in the afternoon, to be next morning restored to its place in the collection on the shelves. No one went into this room, which is in a locked portion of the building, before the following day. The temperature was moderate—about 20° or 22° C.—and differed but little from that of the lecture room. The place on the table occupied by the bottles did not receive any direct rays of the sun.

On coming into the room in the morning, a strong odor of chloral at once drew attention to the table, where a circle of half a meter or so in diameter was covered with a thin crust of white meta-chloral. The remains of the sealed vial were found as small fragments scattered about the room, some of

them as much as two or two and a half meters away from where the vial had stood, and some of them on the shelves at a higher level than the top of the table, showing clearly that the vial had not fallen down, or been knocked over by a mouse or rat, but had burst, and with some considerable force, although no other bottle standing near it had been broken.

It seems that polymerization must have taken place so rapidly, and to so large an extent that the heat evolved in the unison of the smaller into larger molecules raised the temperature of the remaining liquid chloral to a point at which the tension of its vapor was more than the vial could withstand.

If this explanation be accepted, the occurrence is in three respects noteworthy. In the first place, the amount of heat evolved in the polymeric change must have been quite large to produce the effect observed, remembering that liquid chloral is only about as volatile as water—has about the same boiling-point under atmospheric pressure ; I do not know of any recorded measurements of the thermal value of the change in question. Secondly, the polymeric change must have occurred with a degree of suddenness which is surprising in view of the very gradual transition from liquid chloral to meta-chloral which is usually observed—other specimens, prepared in this laboratory, have taken several years to become entirely solid. Thirdly, it is not easy to imagine what cause can have provoked this sudden polymerization, there having been less mechanical agitation, less change of temperature, less external disturbance of any kind that can be pointed out, at the time when the change occurred than the specimen had previously been exposed to.

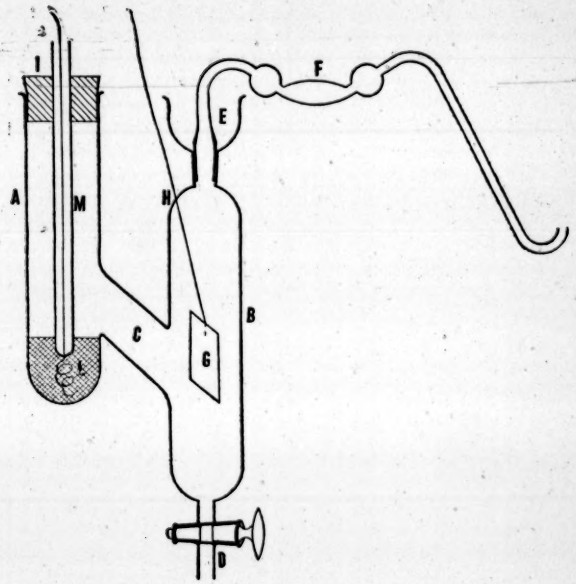
UNIVERSITY OF VIRGINIA,
August 27, 1897.

A NEW FORM OF HYDROGEN GENERATOR.

BY E. W. MAGRUDER.

Several difficulties have been experienced in using Bunsen's hydrogen generator, to overcome which the following apparatus has been devised.

The apparatus (see figure) consists of a tube *A*, closed at the bottom, and connected by means of the inclined side tube



C with the tube *B*, which is furnished at the bottom with the stop-cock *D*, and at the top with the funnel *E*, into which fits with a ground joint the delivery-tube *F*. Tube *B* also contains the platinum electrode *G*, opposite the side tube, suspended by a platinum wire fused through the tube at *H*. Zinc amalgam is put into *A* until it nearly reaches the tube *C*. *A* is closed with a rubber stopper *I* carrying a glass tube *M* containing a platinum wire fused through the tube at *L*. The wire dips into the amalgam. The apparatus may be simplified by leaving off the stop-cock *D*, and by fusing the delivery-tube *F* directly to the top of *B*. The apparatus thus made would be cheaper and for many purposes equally good.

The apparatus is suspended in a battery-jar, filled with

water, by means of a wooden block which clamps the apparatus at the top and rests at the top of the jar.

The objections to the Bunsen form are the following: (1), the uncertainty of obtaining hydrogen free from oxygen, for if oxygen escapes from the amalgam it must of necessity mix with the hydrogen; (2), if the zinc is impure, and volatile hydrogen compounds should be formed, they will mix with the hydrogen; (3), the clogging of the apparatus caused by the formation of zinc sulphate which remains at the bottom covering the amalgam and thus preventing fresh acid from coming in contact with the zinc.

The first and second objections are overcome by having the oxygen and hydrogen electrodes in separate tubes; if oxygen or any other gas escapes it simply rises to the surface in tube *A* and does no harm, as it cannot mix with the hydrogen in *B* without first passing down the side tube *C*, a path which it is hardly likely to follow.

The third objection is overcome by having the amalgam nearly up to the side tube, down which the zinc sulphate flows as soon as formed into *B*, from which it can be drawn off through the stop-cock. This adds greatly to the ease of cleaning the apparatus.

Tests made with the gas generated showed that it is perfectly pure hydrogen.

The apparatus can be obtained from Mr. Emil Greiner, of New York.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
JUNE, 1897.

NOTES.

VICTOR MEYER.

The distinguished Professor of Chemistry in the University of Heidelberg, Germany, died suddenly on the 8th of August. Victor Meyer was born on the 8th of September, 1848, in Berlin. At the age of sixteen he entered the University of Berlin after having completed a preliminary course of study in a "Gymnasium." After one semester at Berlin he went to Heidelberg to work under Bunsen, whose successor he became in later years. He received his degree from the University of Heidelberg, and then returned to Berlin to continue his

studies under Von Baeyer. In 1871 he was called to Stuttgart as first assistant to Von Fehling at the Polytechnic Institute, and was given the title of Professor of Organic and Theoretical Chemistry. A year later he was appointed Professor of General Chemistry in the Polytechnic Institute of Zurich. Here he remained for twelve years. In 1885 he succeeded Hübner as Professor of Chemistry at Göttingen, and four years later he was called to Heidelberg.

He was one of the most active and brilliant chemists of his time, and he was most successful in his work. Probably no other chemist has done more to enlarge the boundaries of chemistry and to clear up dark places during the past quarter of a century than Meyer. Among the many important investigations carried out by him and his students, the following may be mentioned: When he began his career there was a good deal of confusion in the classification of the di-derivatives of benzene. By the application of a reaction devised by him—the fusion of a sulphonate with an alkali formate—he was able to show that salicylic acid, which had been regarded as a meta compound, belongs in reality to the ortho series. This led to important consequences. Shortly afterward he brought to light and thoroughly examined the aliphatic nitro compounds. In the course of this work he discovered the isonitroso compounds, and showed that they are oximes. The study of the oximes led to their preparation by the treatment of aldehydes and ketones with hydroxylamine, and the foundations of the stereochemistry of nitrogen compounds were thus laid. He devised a simple method for the determination of vapor densities—a method that has come into general use. In the application of this method he showed that when the vapor of iodine is heated to a high temperature its density becomes less and less until finally it is such as to show that the iodine molecules have been split into two atoms each. At least that is the simplest conclusion to be drawn from the facts established. He discovered thiophene in benzene, and worked out its chemistry and that of its homologues and derivatives in a marvelously perfect way. Thiophene is, in fact, said to be one of the most thoroughly studied substances.

Within the last few years he has been engaged in the investigation of the iodoso compounds and the iodonium bases, both of which classes of substances awakened the interest of chemists to an unusual degree. The "Lehrbuch der organischen Chemie," written by himself and Jacobson, is the most interesting and valuable text-book of this subject now available.

It is generally stated that the indirect cause of his death

was over-work. He had been warned repeatedly to spare himself, but his inborn desire for activity seems to have been uncontrollable.

PAUL SCHÜTZENBERGER.

M. Paul Schützenberger died in Paris, June 28th, 1897. He was born in Strasbourg, Dec. 23rd, 1829, and received his doctorate from that university at the age of twenty-six. He turned his energies to chemistry, and was appointed to that chair in the high school ot Mühlhausen. Later he became sub-director of the chemical laboratory at the Sorbonne, and in July, 1876, was called to the leadership of chemistry at the Collége de France. He became a member of the Academy of Medicine in 1884, and in 1888 was accorded the distinguished honor of membership in the Paris Academy of Sciences, having been elected to the position made vacant by the death of M. Débray. M. Schützenberger has written a number of books, the best known being: Chimie appliquée à la Physiologie Animale et au Diagnostic Médical (1864); Des Matières Colorantes (1866); Les Fermentations (1875), which has been translated into English and published in the International Science Series; and Traité de Chimie Générale (1879). He has published also a large number of papers describing his researches on vegetable alkaloids, the constitution of the albumins, and on various inorganic substances.

Chemistry has lost from her ranks, in M. Schützenberger, one of her most active workers. H. C. J.

C. REMIGIUS FRESENIUS.

The head of the well-known laboratory at Wiesbaden, Germany, died June 11, after a long life devoted to work in the field of analytical chemistry. Fresenius was born in the year 1818. After studying at Bonn he became Privatdocent in Liebig's laboratory at Giessen, in 1841. In 1845 he went to Wiesbaden, and there he remained active until his death. At first he was Professor of Chemistry at the Agricultural Institute, but in 1848 he opened an independent laboratory for instruction. His famous books on Qualitative and Quantitative Analysis and many of his contributions to analytical chemistry are well-known to chemists. His *Zeitschrift für analytische Chemie* has also served to keep his name prominently before the chemical world, and to further the interests of his chosen subject.